DEVELOPMENT AND USE OF COMPUTER TECHNIQUES IN X-RAY CRYSTALLOGRAPHIC STUDIES

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ABBREVIATIONS

Ac	acetyl
Bu^t	t-butyl
Bz	benzoyl
CNDO	complete neglect of differential overlap
DBC	diffracted beam collimator
E	normalised structure factor
e.s.d.	estimated standard deviation
Et	ethyl
F_c	calculated structure factor
F_o	observed structure factor
ir	infra-red
Me	methyl
nmr	nuclear magnetic resonance
pmr	proton magnetic resonance
Ph	phenyl
Pr^i	isopropyl
TCNE	tetracyanoethylene

ABSTRACT

The crystal and molecular structures of four chemically unrelated compounds have been determined by X-ray crystallography. One compound is organometallic and it crystallises in a centrosymmetric space group while the others are organic and their space groups are non-centrosymmetric.

The compound bis(triphenylarsine)hexafluorobuta-1,3-diene platinum crystallises in two forms. Traditional vector methods were used to solve the structure of the isomer reported here. This is a further example of an organometallic compound where an olefin, in this case hexafluorobutadiene, is co-ordinated to the metal atom by one olefin bond to form what may be described as a 'metallo-cyclopropane' ring.

Direct methods were used to determine the structures of 1,1-dichloro-2,5-diphenylcyclopropabenzene and 4,5,6-tri-O-benzoyl-2,3-di-S-ethyl-2,3-dithio-D-allose diethyl dithioacetal. In the first of these compounds the cyclopropabenzene system is not quite planar and the phenyl substituents are twisted and bent from the plane of the benzene ring in the cyclopropabenzene system. The second of these analyses confirmed the molecular configuration of the tetra-thio aldose derivative as D-allo and established that the molecule has a bent-chain conformation similar to that found in solution.

The conformation of a brominated compound, extracted as an acetate derivative of formula $C_{32}H_{55}O_8Br$ from the seaweed species Laurencia thyrsifera, has been established. The compound's structure is related to squalene and was solved using Vector methods.

In addition to these analyses unsuccessful attempts to solve the crystal structures of a dinitro-imidazole derivative ($C_4H_4N_4O_4$) and a compound thought possibly to be a tetracyclo-decane ($C_{15}H_{12}N_4$) are outlined.

A significant part of this project involved the further development of the X-ray crystallographic program suite of the University of Canterbury which is used in all X-ray structure analyses. Particular projects contributing to this development are discussed.

CHAPTER 1

INTRODUCTION

This thesis is concerned with two interconnected areas of study. The first of these is the investigation of new computing techniques and the further development of the existing library of computer programs for X-ray crystal structure analysis at the University of Canterbury. The second is the parallel application of the library to the solution of four crystal structures and the attempted solution of two others.

A general description of the experimental and computing methods employed in crystal structure solutions is given in Chapter 2. Chapters 3 to 7 discuss specific structure analyses in detail. Chapter 8 is a review of the development of the crystallographic program suite implemented on the Burroughs B6718 computer including consideration of particular problems associated with this specific computer architecture.

1.1 COMPUTER PROGRAMMING

The computing developments undertaken in this laboratory by several persons, including the author, have two objectives. Firstly, to facilitate solution of the larger, more complex, and frequently more difficult crystal structures. Secondly, to reduce the computing expertise required during routine crystal structure analyses. (Often

inexperienced crystallographers who are only wanting to do a single structure determination.)

The arrival at the University of Canterbury of the Burroughs B6718 computer, which coincided with the initiation of this project in February 1973, greatly extended the scope of computing activities. Prior to this time the main University computer was a very heavily used IBM 360/44 with very limited back-up storage. The conversion of the X-ray crystallographic program suite from the IBM 360/44 to the Burroughs B6718 was a sizeable task involving a number of people. It was at least a year before all the programs were working in a satisfactory manner. In addition to the actual program conversion a fresh approach to solving crystal structures had to be developed. This development is still proceeding with a shift of emphasis towards interactive computing activities. Inadequacies in the service available at interactive terminals have severely hampered this work.

X-ray intensity data are collected in this laboratory using a Hilger and Watts four-circle diffractometer controlled by a DEC PDP8 computer. During the course of this project the computer has been upgraded from a PDP8/I with a Tennecomp cartridge system to a PDP8/f eventually equipped with a twin-drive floppy-disk unit. The author contributed to the necessary software developments during these changes.

1.2 CRYSTAL STRUCTURE ANALYSES

The crystal structure analyses presented in this thesis are those of chemically, totally unrelated compounds. Prior

to the start of this project, crystal structure determinations where the space-group was non-centrosymmetric proceeded routinely in this laboratory, only in those cases where traditional 'heavy atom' methods were successful. Subsequently, the implementation of the well-known 'direct methods' program MULTAN (Main, Woolfson and Germain, 1971) has greatly improved the chance of success with the more difficult structures not amenable to Patterson synthesis approaches. For this reason it was decided to concentrate attention, initially, on the determination of the structures of 1,1-dichloro-2,5-diphenylcyclopropabenzene ((Chapter 4), (Halton, McLennan and Robinson, 1976)) and the tetra-thio-allose derivative, 4,5,6-tri-O-benzoyl-2,3-di-S-ethyl-2,3-dithio-D-allose diethyl dithioacetal ((Chapter 5), (McLennan, Robinson, Bethell and Ferrier, 1977)), for which full sets of data were already available. Interest in these problems had been stimulated by Dr. B. Halton and Professor R.J. Ferrier, respectively, both of Victoria University of Wellington. The solution of both these structures proved quite challenging.

The structure analysis of bis(triphenylarsine)hexafluorobuta-1,3-diene platinum (Chapter 3) was supervised by Professor B.R. Penfold, who with his co-workers, has been concerned with structural studies of a range of low-valent metal-fluorocarbon complexes. The crystals for these analyses have been supplied by Professor F.G.A. Stone of the University of Bristol. The reasons for undertaking this analysis, while still occupied by the determinations of the two structures above, were two-fold. Firstly, preliminary

studies of crystals of formula $(AsPh_3)_2PtC_4F_6$ by Professor B.R. Penfold and R.G. Holloway, had established the existance of more than one crystalline form. Unfortunately, the isomer whose structure was determined (Holloway, 1973) was considered to be a minor product of the reaction system under study. Thus the determination of the structure of the other isomer was considered an urgent problem. Secondly, the large but straight forward heavy-atom nature of these problems meant they were very suitable for testing various aspects of the conversion of programs from the IBM 360/44 computer to the Burroughs B6718 computer.

Crystals for structure analysis, of the compound known as thyrsiferyl acetate ($C_{32}H_{55}O_8Br$), were supplied by Dr. M.H.G. Munro of this University. The compound was the high molecular weight acetate derivative isolated from the ether soluble oil extracted from a red algae seaweed species, Laurencia thyrsifera. It was of considerable interest as little was known about its structure, other than its formula, and that it was a saturated, mono-brominated tetra-cyclic ether, containing rings of unknown size. The size of this molecule and the space group ($P2_1$) rendered it appropriate for program development testing. The structure solution and refinement of thyrsiferyl acetate (Blunt, Hartshorn, McLennan, Munro, Robinson and Yorke, 1977) is presented in Chapter 6.

Chapter 7 outlines attempts at two further structural analyses which were not successful. The first of these, the structure of the imidazole derivative ($C_4H_4N_4O_4$) was referred to this author by Dr. M.C. Couldwell, then of the

University of Otago. The reason for difficulty with this small light atom problem is without doubt the very poor quality of the intensity data available. The other problem, for which a reasonably good set of intensity data was collected is the structure analysis of a tetra-cyclic decane derivative with the empirical formula $C_{15}H_{12}N_4$. The space group is $P2_1/c$ but there are three molecules in the asymmetric unit. Initial attempts to solve this structure using statistical methods were expensive and unsuccessful. As the problem was too large to be suitable for testing new program developments and it also appeared that the solution could prove too expensive, it was decided not to pursue this analysis further. Attention was concentrated on the solution of thyrsiferyl acetate instead.

CHAPTER 2

EXPERIMENTAL PROCEDURES IN X-RAY STRUCTURE ANALYSES

2.1 COLLECTION AND REDUCTION OF INTENSITY DATA

The procedures used in the intensity data collection and primary processing were the same for all six compounds studied, including the two where the data were not collected by the author. As most of the techniques used are very similar to those used in other laboratories, discussion is confined to a brief description of a typical analysis. Experimental details for particular analyses are given subsequently in the appropriate chapter.

2.1.1 Preliminary Investigation

The crystals were initially examined by Weissenberg or precession photography to ensure they were of suitable quality for further investigation. From this preliminary study the approximate unit cell constants and possible space groups were established. The density of the crystals, where it was measured, was obtained by either the flotation method or using a calibrated density gradient column as described in 'International Tables for X-ray Crystallography' Vol.III (Richards and Berger, 1962). A single crystal for diffractometry was selected after examination by precession photography. It was mounted on a goniometer head in a random orientation to minimise the incidence of multiple reflections (Renninger, 1937). Care was always taken to ensure the mounting was rigid.

2.1.2 Collection of Intensity Data

All sets of intensity data were collected on a Hilger and Watts computer-controlled four-circle diffractometer. Preparation for an automatic data collection involved establishing the crystal orientation precisely and also accurate unit cell parameters. The approximate crystal orientation was determined by re-establishing the setting angles for several reflections which had been absolutely indexed previously from precession photographs. An initial orientation matrix was formed from these angles for two reflections and used to calculate the setting angles of intense reflections throughout reciprocal space.

Accurate unit cell and orientation parameters were obtained by least-squares refinement (Busing and Levy, 1967) using as observations values of ω, 2θ and χ for up to 12 reflections. The setting angles of these centred reflections were obtained automatically by a modification of the procedure of Busing (1969). The angles varied were ϕ, χ and 2θ and bisecting mode geometry ($\theta = \omega$) was used. The diameter of the diffracted beam collimator (3.5 or 5 mm) precluded accurate resolution of $K\alpha_1$ and $K\alpha_2$ peaks. Hence, the wavelength used in refinements was $K\bar{\alpha}$, the weighted mean of the $K\alpha_1$ and $K\alpha_2$ components. Parameters were considered to have converged to their best values when the difference between the observed and calculated setting angles for all reflections were less than 0.03° and estimated standard deviations for the diffractometer orientation defining angles were less than 0.01°. While this precision was usually readily achieved, lower standards were adopted in the thyrsiferyl acetate data collection.

The mosaicity of the crystal was examined by means of open-counter ω-scans (Furnas, 1957) at a take-off angle of 3°, and was considered to be very good when peak widths at half-height for strong low angle reflections were in the range 0.05° to 0.2°.

Intensities of all reflections were recorded using the ω-2θ scan technique. The incident X-radiation was filtered with the appropriate β-filter. The scans were symmetric and centred on the peak position calculated from the wavelength of $K\bar{\alpha}$ radiation. Scan steps were usually set at 0.02° in 2θ and 0.01° in ω, except for the thyrsiferyl acetate collection where they were 0.04° and 0.02°, respectively. Appropriate scan widths were determined experimentally for each crystal. Stationary crystal, stationary background counts were taken at both ends of the scan range. The distance from the crystal to the receiving aperture of the diffracted beam collimator (DBC) was permanently fixed at 230 mm and all intensity data were collected using a 5 mm DBC.

Calibrated attenuators were used to bring strong reflections within the linear response range of the scintillation counter whenever rates exceeded 8,000 counts/sec. Throughout the data collections the intensities of three strong reflections were measured regularly and subsequently used to produce correction factors for non-statistical variations in intensity due, for example, to crystal decomposition.

2.1.3 Reduction of Intensity Data

Data processing was carried out as described by

Corfield, Doedens and Ibers (1967) using the local program HILGOUT (Dellaca, 1970). The integrated intensity was given by

$$I = C-0.5(t_c/t_b)(B_1+B_2)$$

where C is the scan count, t_c and t_b are scan and background times and B_1 and B_2 are the background counts. The standard deviation for each measured intensity was

$$\sigma(I) = (C+0.25(t_c/t_b)^2(B_1+B_2)+(pI)^2)^{\frac{1}{2}} \qquad (2.1)$$

where p is a factor, initially assigned a value of 0.05, introduced to avoid overweighting more intense reflections (Grant, Killean and Lawrence, 1969). Lorentz and polarisation corrections were applied to I and $\sigma(I)$ to obtain values of F_o^2 and $\sigma(F_o^2)$.

In cases where more than one symmetrically equivalent member of the form was collected, these data were averaged. The standard deviation of the average intensity $\sigma(F_o^2)$ was derived statistically from the individual contributing e.s.d.'s unless this quantity was less than the range of F_o^2 values. In this case the range was taken as an appropriate e.s.d. to give low weight to the inaccurate intensity during refinement. All e.s.d.'s were multiplied by $(1/NEQ)^{\frac{1}{2}}$ where NEQ was the number of times a reflection was actually observed (Robinson and Ibers, 1967).

The standard deviation of each intensity was required to compute the weighting factor, $w = 4F_o^2/\sigma(F_o^2)^2$, which was used in the least-squares minimisation of the function

$$\Sigma w(|F_o|-|F_c|)^2 \qquad (2.2)$$

where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes, respectively. In the final stages of refinement the p-factor, in Exp. (2.1), was adjusted so that the function (2.2) showed as little as possible dependence on $|F_o|$, $\sin\theta/\lambda$ and reflection indices (Cruikshank, 1965).

Absorption corrections were applied, where necessary, by the analytical method of de Meulenaer and Tompa (1965) using program ABSORB (Templeton and Templeton, 1973). Input to this program consisted of indices of boundary faces of the crystal and perpendicular distances of these from an origin within the crystal. The program plots the calculated points of intersection of all the boundary faces as a check that the size and shape of the crystal have been correctly defined.

2.2 SOLUTION AND REFINEMENT PROCEDURES

The initial models for the crystal structure analyses described in this work were developed by way of Patterson syntheses, direct methods or a combination of the two. The expansion of initial models into complete structural models proceeded via Fourier syntheses combined with full-matrix least-squares refinements. Computational aspects of these techniques are discussed separately below, while details for particular analyses are given in the following chapters.

All calculations were performed on either the IBM 360/44 computer or the Burroughs B6718 computer at the University of Canterbury. Diagrams drawn on the Calcomp plotter were generated by the local version of program ORTEP (Johnson, 1970).

2.2.1 The Patterson Function

Analyses of Patterson syntheses (Patterson, 1935) were part of all the successful analyses reported in this thesis. The location of heavy atoms from such syntheses in two analyses ($(AsPh_3)_2\overline{PtCF_2CFCFCF_2}$ and $C_{32}H_{55}O_8Br$) was sufficient to resolve these phase problems. In the other two successful analyses, the Patterson syntheses were used to help discriminate between possible structural models which had been obtained from direct methods.

The Patterson function, which only involves the square of the amplitudes and not the phases of the structure factors, is commonly written in the Fourier series form as

$$P(u,v,w) = V^{-1}\sum_{hkl}\sum\sum|F_{hkl}|^2\cos 2\pi(hu+kv+lw)$$

where V is the unit cell volume. This function shows maxima at (u,v,w), corresponding to interatomic vectors between all pairs of atoms at (u+x, v+y, w+z) and (x,y,z) in the unit cell. It a unit cell contains N atoms, there are N^2 vectors in the Patterson synthesis. N of these vectors are of zero magnitude being vectors from each atom to itself and coalesced at u=v=w=0. There are thus N^2-N non-origin peaks in a Patterson calculation. Because of the requirement to pack N^2-N rather than N peaks in the unit cell, there is a greater degree of overlap among the peaks of the Patterson map than of an electron density map. This effect is further accentuated by the larger intrinsic breadth of the Patterson peaks. To improve the resolution, use is often made of the sharpening process (using program SHNORM which is based on programs NRC-4 (Hall, 1968) and NRC-5 (Huber and Brisse, 1970))

which involves modification of F^2_{hkl} such that dependence of the atomic scattering factors on $\sin\theta/\lambda$ and the effects of thermal vibrations are removed (Burger, 1959, 1960).

2.2.2 Direct Methods

"In its common usage 'direct structure determination' implies the use of procedures involving direct phase determination i.e. the determination of structure by use of the intermediate step of evaluating the phases of the diffraction amplitudes directly from the scattered intensities." (J. Karle, 1976). Over a number of years, special mathematical relationships and properties of the phases of structure factors, have been discovered and the procedures of structure solution by direct methods have been developed. These developments were the work particularly of Harker and Kasper (1948), Sayre (1952), Cochran and Woolfson (1955), Zachariasen (1952), and Karle and Hauptman (1956). More recently, Karle and Karle (1966), Karle (1971) and Germain, Main and Woolfson (1970, 1971), and their co-workers have made these methods particularly appropriate to many space groups.

The program MULTAN (Main, Woolfson and Germain, 1971) was used in the solution of the two structures obtained by direct methods ($C_6H_2(CCl_2)Ph_2$ and $C_{35}H_{42}O_6S_4$). Normalised structure factor magnitudes ($|E|$'s) were input to the program. They were obtained from application of the formula

$$|E_{\underset{\sim}{h}}|^2 = \frac{|F_{\underset{\sim}{h}}|^2}{\epsilon \sum_{j=1}^{N} f^2_{j\underset{\sim}{h}}}$$

where $\underset{\sim}{h}$ is a vector of the form (h,k,l)*, $|F_{\underset{\sim}{h}}|$ is the observed structure factor magnitude, $f_{j\underset{\sim}{h}}$ is the atomic scattering factor for the jth atom in the unit cell and ε is a number which corrects for space group extinctions. The |E|'s were calculated by program SHNORM.

The first stage in the phase determination process is the generation of triplets of reflections satisfying the Σ_2 relationship

$$\phi_h = \phi_{h'} + \phi_{h-h'}$$

where ϕ_h is the phase associated with the normalised structure factor E_h. The set of triplets is then used in the very important process of determining a starting set of reflections for the tangent refinement procedure. This starting set is made up of three types of reflections.

(i) High |E| reflections whose phases have been established with high probability (>90%) from Σ_1 relationships of the general form:

$$s(E_{2h2k2l}) = S(|E_{hkl}|^2-1)$$

This basic formula must be modified to take space group symmetry into account but it is applicable to non-centrosymmetric space groups as well as centrosymmetric space groups (Hauptman and Karle, 1953).

(ii) Origin and enantiomorph (in the case of a non-centrosymmetric crystal) defining reflections whose phases will be fixed in accordance with the restrictions imposed by the space group symmetry.

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* In subsequent expressions $\underset{\sim}{h}$ will be written for convenience as h.

(iii) Two or three further reflections chosen, as far as possible, to be in different parity groups and to lead quickly to multiple indications for unknown phases.

The multiple starting point to the tangent refinement comes from the reflections of type (III) above, in the starting set. These are assigned initial phases of all possible combinations of $\pm\pi/4$ and $\pm 3\pi/4$ or in the case of centric reflections, 0 and π.

Beginning with the starting set described above, phases of other reflections are determined and refined using a weighted tangent formula (Germain, Main and Woolfson, 1971a).

$$\tan\phi_h = \frac{\sum_{h'} w_{h'} w_{h-h'} |E_{h'} E_{h-h'}| \sin(\phi_{h'} + \phi_{h-h'})}{\sum_{h'} w_{h'} w_{h-h'} |E_{h'} E_{h-h'}| \cos(\phi_{h'} + \phi_{h-h'})} = \frac{T_h}{B_h}$$

where w_h is a weight associated with the phase ϕ_h and each weight is computed from

$$w_h = \tanh(0.5\alpha_h) \qquad \text{and}$$

$$\alpha_h = |E_h|(T_h^2 + B_h^2)^{\frac{1}{2}}$$

In the initial cycles of tangent refinement the phases of all reflections in the starting set are kept constant but in the final iterations those of the reflections of type (iii) are allowed to refine.

For each set of phases determined from the multiple starting point, 'figures of merit', which are measures of the reliabilities of the phases assigned, are measured. The phase sets with the best figures of merit can be used in the calculation of E-maps (Section 2.2.3b below). A structure

factor calculation can be initiated using atomic positional parameters determined from the high peaks in such a synthesis.

2.2.3 Fourier Syntheses

Fourier syntheses, especially difference Fourier syntheses, were used regularly in all structure solving attempts. Syntheses were usually calculated in three-dimensions and the function evaluated for unique asymmetric units in sections through the cell. Points were sampled at regular intervals, about 0.3Å, parallel to each cell axis. Peak positions and peak heights were also listed by program FOURIER (Zalkin, 1965). Alphanumeric plots and electron density contouring were optional routines in this program.

2.2.3a Difference Fourier Synthesis

In a difference Fourier synthesis, the coefficients used are the differences between observed and calculated structure factors, $|F_o|$ and $|F_c|$, and α_c is the phase angle computed from the trial structure. The series may be expressed in the form

$$\Delta\rho(x,y,z) = V^{-1}\sum_{hkl}\sum\sum(|F_o|-|F_c|)\exp(i\alpha_c)\exp(-2\pi i(hx+ky+lz)).$$

Likely improvements in the structural model (atom positions or better atomic descriptions) are suggested by the maxima in this function.

2.2.3b Observed-Fourier Synthesis

The Fourier series used for computing electron densities is

$$\rho(x,y,z) = V^{-1}\sum_{hkl}\sum\sum|F_o|\exp(i\alpha_c)\exp(-2\pi i(hx+ky+lz))$$

where the terms are as defined above.

The electron density thus evaluated may yield positions of atoms which can be added to the trial model and least-squares refinements may follow. This Fourier synthesis is particularly useful in the early stages of developing a trial model, and it was used with success in the analyses where the space group was non-centrosymmetric. An E-map can be regarded as an observed Fourier synthesis where the coefficients are |E|'s rather than |F|'s. It is calculated following phase determination by direct methods and atomic parameters may be derived from it as they are from a normal F_o synthesis.

2.2.4 Structure Factor Calculations and Least-Squares Refinements

The method of least-squares used in the structure refinements involved minimising the weighted sum of the squares of the differences between the observed and calculated structure factor amplitudes respectively:

$$\Sigma w(|F_o|-|F_c|)^2$$

where w is the weight calculated at $4F_o^2/\sigma(F_o^2)^2$.
The conventional R-factors, which are convenient parameters for measuring the correctness of a structure, are defined as

$$R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o| \quad \text{and}$$

$$R_2 = (\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2)^{\frac{1}{2}}.$$

The positional parameters of atoms of the initial models, located by inspection of the Patterson or E-map synthesis, along with thermal parameters were refined by the full-matrix least-squares method. Model building proceeded

by successive Fourier syntheses to locate further atoms with intermediate least-squares refinement of parameters.

Structure factor calculations and least-squares refinements were performed by program CUCLS, the local version of the well known program ORFLS (Busing, Martin and Levy, 1962). Unfortunately, the limitations of computer memory required that the maximum number of parameters varied in any calculation should not exceed 176.* In two analyses ($C_6H_2(CCl_2)Ph_2$ and $C_{35}H_{42}O_6S_4$) each parameter set was split into two large blocks to enable the large refinement calculations to proceed.

The equation for the calculated structure factor may be expressed as

$$F_{ch} = \sum_{j=1}^{N} f_{jh} T_{jh} \exp(2\pi i \mathbf{h} \mathbf{r}_j)$$

where h is the scattering vector, f_{jh} is the atomic scattering factor, T_{jh} is a function describing thermal effects, and vector r_j is the position of the jth atom in the unit cell of N atoms.

(i) f_{jh}. The atomic scattering factors of non-hydrogen atoms used in this work were those of Cromer and Mann (1968). For hydrogen atoms the tabulation of Stewart, Davidson and Simpson (1965) was used. For elements heavier than fluorine, corrections for the effects of anomalous dispersion were made to F_c in the following way. If f_o is the normal scattering factor then that for the anomalous scatterer may be written as

$$f_a = f_o + \Delta f' + \Delta f''.$$

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* Recently this has been relaxed to allow 360 refined parameters.

The real and imaginary components $\Delta f'$ and $\Delta f''$ applied were those of Cromer (1965). In centrosymmetric space groups a non-zero $\Delta f''$ for any atom in the structure causes the structure factor to become complex, although Friedel's law still holds. On the other hand, any non-zero $\Delta f''$ in a non-centrosymmetric space group leads to the breakdown of Friedel's law. This may be used to distinguish between absolute molecular configurations (Bijvoet, Peerdman and Van Bommel, 1951; Ibers and Hamilton, 1964).

(ii) T_{jh}. Each atom was assumed to be vibrating in a centrosymmetric potential field, and assigned either isotropic or anisotropic thermal parameters as appropriate. For the isotropic case the appropriate expression is

$$T_{jh} = \exp(-B(\sin\theta/\lambda)^2)$$

where $B = 8\pi^2U$ and U is the mean-square amplitude for vibration (in Å^2). For anisotropic vibration the termperature factor expression is

$$T_{jh} = \exp(-2\pi^2(U_{11}h^2a^{*2}+U_{22}k^2b^{*2}+U_{33}l^2c^{*2}+ 2U_{12}hka^*b^*+2U_{13}hla^*c^*+2U_{23}klb^*c^*))$$

where U_{ij} are the thermal parameter terms of mean-square amplitudes of vibrations (in Å^2).

CHAPTER 3

STRUCTURAL STUDY OF BIS(TRIPHENYLARSINE)HEXAFLUOROBUTA-1,3-DIENE PLATINUM

3.1 INTRODUCTION

Hexafluorobuta-1,3-diene reacts with $Fe(CO)_5$ (Hunt, Roundhill and Wilkinson, 1967), $Ni(AsMe_2Ph)_4$ (Browning, Green and Stone, 1971), $Ni(CNBu^t)_4$ (Green, Shakshooki and Stone, 1971) and $PtPr^i_2(C_8H_{12})$ (Browning, Empsall, Green and Stone, 1973) to give complexes the ^{19}F nmr of which are interpretable only if the $\overline{MCF_2CF=CFCF_2}$ (M=Fe, Ni or Pt) group is present, since two signals are observed of relative intensity 2:1. An X-ray crystallographic study of the iron compound has been reported (Hitchcock and Mason, 1967).

A study of the reaction of $Pt(AsPh_3)_4$ with hexafluorobuta-1,3-diene has also been made. In contrast to the above results, the ^{19}F nmr spectrum of the product contained six signals of equal intensity and was only consistent with a 'metallo-cyclopropane' structure $(AsPh_3)_2\overline{PtCF_2CFCF=CF_2}$ (Maples, Green, Stone and Spencer, 1974). However, the solid state ir spectrum showed two bands characteristic of a free olefin function $-CF=CF_2$. In solution only one of the bands was intense while the other appeared as a weak shoulder. Since this compound has been used in tin (IV) halide promoted vinyl rearrangements a crystal structure analysis was thought necessary to characterise it.

The crystals were found to be of two forms. When the first form was structurally characterised as $(AsPh_3)_2\overline{PtCF_2CF=CFCF_2}$ (Holloway, 1973), the second form was tentatively assigned the structure $(AsPh_3)_2\overline{PtCF_2CFCF=CF_2}$. The analysis described below has confirmed this assumption as well as providing another example of three-membered metal-carbon-carbon ring formation in the attachment of an unsaturated fluorocarbon to a metal of the nickel triad (Browning and Penfold, 1973; Stone, 1972; Russell and Tucker, 1975). On the basis of the observation of only the six peaks characteristic of the 'metallo-cyclopropane' isomer in the ^{19}F nmr it has been concluded that the other isomer is a very minor component of the mixture (Maples et al., 1974).

3.2 EXPERIMENTAL

The investigation was carried out on a sample of $(Ph_3As)_2Pt(CF_2CFCFCF_2)$ kindly supplied by Professor F.G.A.Stone of the University of Bristol, Bristol, England. The crystals were prepared by reacting a suspension of tetrakis(triphenylarsine)platinum in benzene with an excess of hexafluorobuta-1,3-diene (Maples et al., 1974). From the colourless crystals two forms, Isomer A and Isomer B, both crystallising in a monoclinic space group were identified (Holloway, 1973). The structure elucidation discussed below is of Isomer B.

Relevant crystal data are summarised in Table 3.1. The preliminary investigations using precession and Weissenberg photography revealed conditions limiting possible reflections

uniquely consistent with space group $P2_1/c$ (0k0, k=2n; h0l, l=2n). It was found convenient to solve the structure in the unconventional setting $P2_1/n$ (equivalent positions x,y,z; -x,-y,-z; $\frac{1}{2}$+x, $\frac{1}{2}$-y, $\frac{1}{2}$+z; $\frac{1}{2}$-x, $\frac{1}{2}$+y, $\frac{1}{2}$-z).

The experimental density was determined using a calibrated density column set up using the liquids bromobenzene and 1,2-dibromoethane.

The crystal used for data collection was of poor quality and irregular geometry, with the approximate dimensions given in Table 3.2. This crystal was obtained by cutting up a larger crystal. It appeared, unfortunately, that the well-formed crystals of the sample were all of Isomer A. The intensity data were collected using zirconium-filtered MoKα X-radiation and the techniques described in Chapter 2. The relevant experimental parameters are given in Table 3.2.

A curious feature of the data collection was a gradual increase up to a maximum of 20% in the count rate of the three standard reflexions monitored at regular intervals. Crystal mis-orientation was eliminated as a possible cause and it is tempting to assume that the crystal quality was actually improving under exposure to X-rays. The data were initially scaled linearly to correct for this increase in intensity.

An unfortunate accident to this crystal, before the measurement and identification of the crystal faces had been made, ruled out the possibility of making an absorption correction. A request was made for another sample of better quality crystals so that the data collection could be

Table 3.1

Crystal Data for $(AsPh_3)_2\overline{PtCF_2CFCFCF_2}$

Formula	$C_{40}H_{30}F_6As_2Pt$
Formula weight	969.61
System	Monoclinic
Space group	$P2_1/n$
a	13.230(4)Å*
b	18.078(4)Å
c	16.786(4)Å
β	113.92(2)°
V	3670.11Å^3
D_{meas}	1.77(3) g cm^{-3}
D_{calc}	1.75 g cm^{-3}
Z	4
F(0,0,0)	1872
μ(MoKα)	59.73 cm^{-1}

*Throughout this thesis the figures given in parentheses are estimated standard deviations in the least significant digit quoted. They were usually derived from the inverse matrix in the course of normal least-squares refinement calculations.

Table 3.2

Experimental Parameters of $(AsPh_3)_2\overline{PtCF_2CFCFCF_2}$

Aproximate crystal dimensions	.38 x .35 x .24 mm^3
Mosaicity	0.19-0.35°
θ scan range	0.90°
Scan time	90 sec.
Total background time	45 sec.
θ limit	20°
Total independent reflections	3425
Reflections used in refinements for which $F_o^2 \geq 3\sigma(F_o^2)$	2007
Weighting parameter p	0.05
Ratio of observations to parameters	14.3

repeated. However repetition of the reaction several times did not result in better quality crystals (Stone, 1973) so that the data were not recollected.

3.3 SOLUTION AND REFINEMENT OF THE STRUCTURE

This structure was solved by conventional heavy atom methods. Positions for one platinum atom and two arsenic atoms were identified from their vectors in a sharpened Patterson synthesis. A structure factor calculation, following refinement of these coordinates and appropriate temperature factors, gave

$$R_1 = 0.225 \quad \text{and}$$

$$R_2 = 0.303.$$

Two difference Fourier syntheses with intermediate refinement and structure factor calculations revealed all but five carbon and fluorine atoms. In subsequent refinements the phenyl rings were treated as rigid hexagonal groups (La Placa and Ibers, 1965; Doedens, 1969) located by defining three positional parameters for the group centroid and three angles for its orientation. These parameters together with a single overall temperature factor were refined for each ring. The remaining five atoms were extracted from two further difference Fourier syntheses.

A final model with anisotropic temperature factors for the platinum, arsenic and fluorine atoms yielded

$$R_1 = 0.073 \quad \text{and}$$

$$R_2 = 0.085,$$

for the 2007 reflections for which $F_o^2 \geq 3\sigma(F_o^2)$. The highest residual peak in a final difference map was 1.66 $e\text{Å}^{-3}$

compared with 2.2 $e\text{Å}^{-3}$ for the last carbon atom located by this technique. No shift in the final cycle of refinement exceeded 0.31σ. The standard error in an observation of unit weight was 2.3. The minimised function showed little systematic dependence on either $|F_o|$ or $\sin\theta$, and a calculation of the structure factors for the weak and unobserved reflections ($F_o^2 < 3\sigma(F_o^2)$), revealed no anomalous discrepancies. The final structure factors are listed in Appendix 2.

Final positional parameters and isotropic thermal parameters (where appropriate) for all atoms other than those of the phenyl rings are given in Table 3.3. Table 3.4 gives the anisotropic thermal parameters of the non-carbon atoms and Table 3.5 the positional parameters for the rigid group (phenyl) atoms.

3.4 DESCRIPTION OF THE STRUCTURE

The crystal structure consists of an assemblage of discrete molecules of bis(triphenylarsine)hexafluorobuta-1,3-diene platinum. The geometry of one molecule is illustrated in Figure 3.1, which also gives the atom numbering scheme. Selected interatomic distances and angles are listed in Tables 3.6 and 3.7. The hexafluorobuta-1,3-diene molecule is associated with the platinum atom by sideways attachment of one C=C bond and the formation of a rigid Pt,C,C ring in which the platinum atom is equidistant from the carbon atoms. (Pt-C(1) and Pt-C(2) are 1.97(4) and 1.98(5), respectively.)

Table 3.3

Positional Parameters (x 10^4) and Isotropic Thermal Parameters for Non-group Atoms of $(AsPh_3)_2\overline{PtCF_2CFCFCF_2}$

	x	y	z	B	U
Pt	1018(1)	940.0(7)	1839.0(7)		
As(1)	-605(2)	1747(2)	1233(2)		
As(2)	719(3)	400(2)	3038(2)		
F(1)	2365(18)	-277(10)	1683(17)		
F(2)	3326(15)	633(12)	2452(19)		
F(3)	1317(18)	541(15)	235(12)		
F(4)	3565(28)	1381(24)	883(26)		
F(5)	1623(20)	2448(17)	1016(16)		
F(6)	3101(38)	2639(24)	880(21)		
C(1)	2333(34)	438(25)	1813(26)	10(1)	0.128
C(2)	1781(38)	964(27)	1041(31)	12(1)	0.158
C(3)	2722(62)	1456(39)	1034(39)	16(2)	0.203
C(4)	2190(65)	1909(52)	888(46)	18(3)	0.227

Table 3.4a

Anisotropic Thermal Parameters (β's, $\times 10^4$) for Non-group Atoms of $(AsPh_3)_2\overline{PtCF_2CFCFCF_2}$. Thermal parameters are in the form

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Pt	123(1)	42.3(5)	63.9(8)	11.1(7)	38.0(7)	-1.3(6)
As(1)	99(3)	43(1)	63(2)	-0(1)	28(2)	0(1)
As(2)	123(3)	44(1)	64(2)	-1(2)	29(2)	1(1)
F(1)	259(29)	42(8)	222(23)	44(12)	111(22)	-8(11)
F(2)	101(18)	88(11)	264(27)	38(11)	16(18)	-60(14)
F(3)	229(26)	146(15)	65(11)	-7(16)	40(14)	-40(11)
F(4)	324(45)	221(32)	350(44)	6(29)	284(41)	20(28)
F(5)	227(30)	109(15)	158(20)	-21(18)	81(21)	15(14)
F(6)	548(73)	180(27)	165(25)	-70(38)	153(35)	-23(21)

Table 3.4b

Anisotropic Thermal Parameter (U's, $\times 10^4$) for Non-group Atoms of $(AsPh_3)_2\overline{PtCF_2CFCFCF_2}$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pt	914	700	762	123	358	-18
As(1)	730	715	747	-5	263	2
As(2)	908	727	768	-7	275	12
F(1)	1920	689	2650	484	1045	-116
F(2)	752	1451	3147	421	155	-840
F(3)	1670	2411	1779	-75	374	-525
F(4)	2404	3633	4170	68	2669	282
F(5)	1682	1810	1888	-228	759	216
F(6)	4063	2984	1967	-779	1442	-324

Table 3.5

Positional ($x10^3$) and Thermal Parameters for Group Atoms of $(AsPh_3)_2\overline{PtCF_2CFCFCF_2}$

	x	y	z	β	U
Ring(1)				7.9(3)	0.100
C(11)	-93	208	3		
C(12)	-126	281	-21		
C(13)	-80	160	-56		
C(14)	-100	184	-140		
C(15)	-145	305	-104		
C(16)	-132	257	-164		
Ring(2)				9.9(4)	0.125
C(21)	-203	138	113		
C(22)	-269	100	37		
C(23)	-368	69	29		
C(24)	-402	75	97		
C(25)	-237	144	181		
C(26)	-336	112	173		
Ring(3)				8.1(3)	0.103
C(31)	-47	265	186		
C(32)	59	290	237		
C(33)	75	356	282		
C(34)	-16	399	276		
C(35)	-138	308	180		
C(36)	-122	374	225		

Table 3.5 contd.

	x	y	z	β	U
Ring(4)				8.5(4)	0.108
C(41)	-21	-46	272		
C(42)	-14	-101	332		
C(43)	-80	-164	306		
C(44)	-155	-171	219		
C(45)	- 95	-54	186		
C(46)	-162	-116	159		
Ring(5)				9.8(4)	0.124
C(51)	204	1	399		
C(52)	265	-52	378		
C(53)	363	-79	442		
C(54)	399	-53	527		
C(55)	239	-27	484		
C(56)	337	0	548		
Ring(6)				9.4(4)	0.119
C(61)	120	102	369		
C(62)	10	223	430		
C(63)	-80	201	448		
C(64)	-123	130	427		
C(65)	56	173	390		
C(66)	-77	80	387		

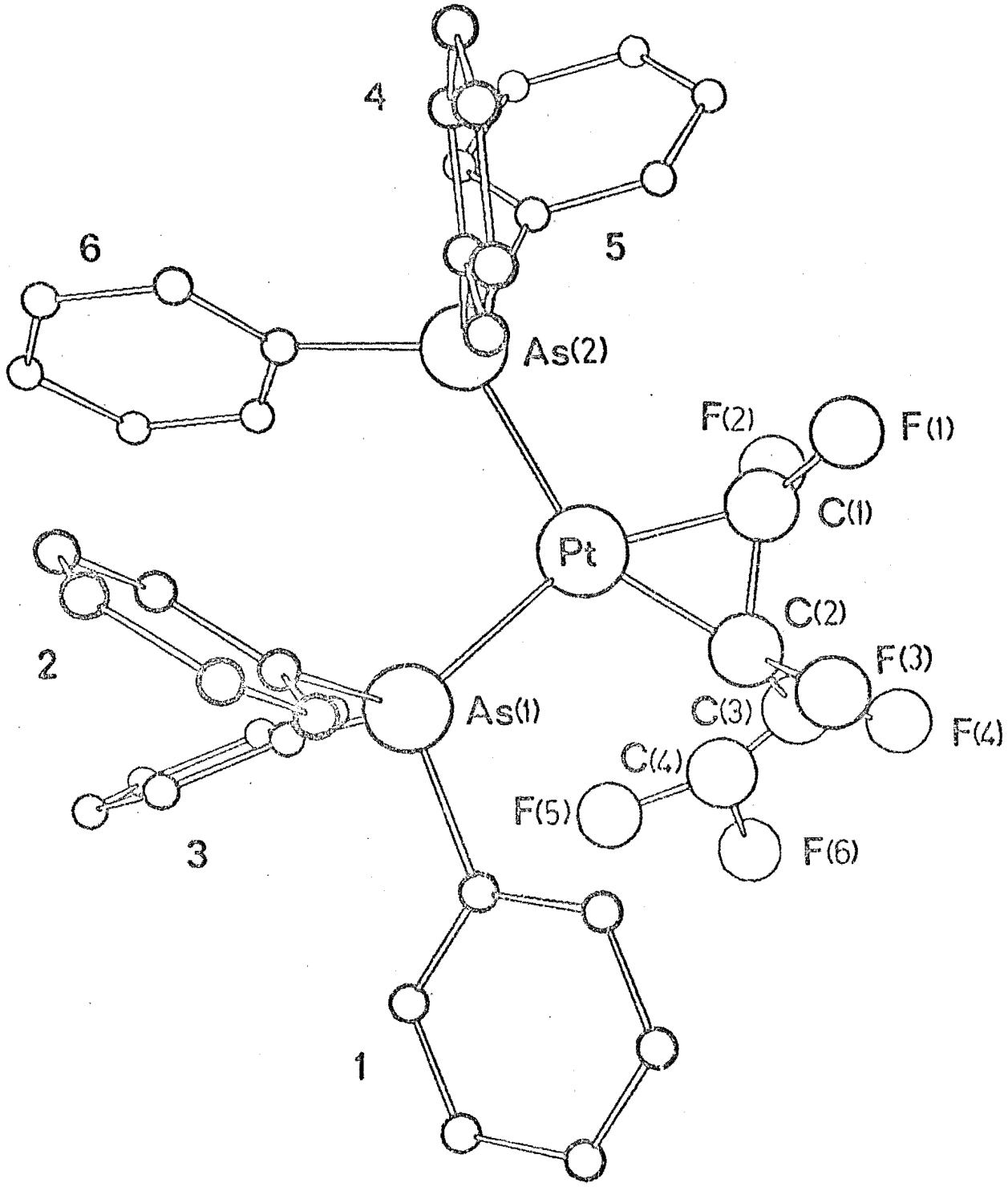

Figure 3.1

A perspective view of one molecule of

$(AsPh_3)_2\overline{PtCF_2CFCFCF_2}$

Table 3.6

Interatomic Distances (Å) in $(AsPh_3)_2\overline{PtCF_2CFCFCF_2}$

Pt-As(1)	2.450(3)	C(1)-C(2)	1.54(5)
Pt-As(2)	2.410(3)	C(2)-C(3)	1.52(7)
Pt-C(1)	1.97(4)	C(3)-C(4)	1.55(8)
Pt-C(2)	1.98(5)		
C(1)-F(1)	1.32(4)	As(1)-C(11)	1.98
C(1)-F(2)	1.36(4)	As(1)-C(21)	1.94
C(2)-F(3)	1.46(5)	As(1)-C(31)	1.92
C(3)-F(4)	1.25(7)	As(2)-C(41)	1.92
C(4)-F(5)	1.30(8)	As(2)-C(51)	1.96
C(4)-F(6)	1.79(8)	As(2)-C(61)	1.95

Table 3.7

Selected Bond Angles (Å) in $(AsPh_3)_2\overline{PtCF_2CFCFCF_2}$

As(1)-Pt-As(2)	100.1(1)	C(1)-C(2)-C(3)	105(4)
C(1)-Pt-C(2)	46(1)	C(2)-C(3)-C(4)	89(8)
As(1)-Pt-C(1)	153(1)		
As(2)-Pt-C(2)	151(1)	F(4)-C(3)-C(2)	138(6)
As(1)-Pt-C(2)	108(1)	F(4)-C(3)-C(4)	127(9)
As(2)-Pt-C(1)	106(1)		
Pt-C(1)-C(2)	67(2)	F(5)-C(4)-C(3)	158(9)
Pt-C(2)-C(1)	67(2)	F(6)-C(4)-C(3)	101(8)
		F(5)-C(4)-F(6)	84(5)
F(1)-C(1)-F(2)	107(3)		
F(1)-C(1)-Pt	123(3)	C(11)-As(1)-C(21)	102.3
F(2)-C(1)-Pt	116(3)	C(21)-As(1)-C(31)	102.2
F(3)-C(2)-Pt	119(3)	C(11)-As(1)-C(31)	103.5
F(1)-C(1)-C(2)	120(4)	C(41)-As(1)-C(51)	101.2
F(2)-C(1)-C(2)	119(4)	C(51)-As(1)-C(61)	100.4
		C(41)-As(1)-C(61)	105.2
F(3)-C(2)-C(1)	109(4)		
F(3)-C(2)-C(3)	110(4)		

The analysis of least-square planes in the molecule (Table 3.8) shows that the co-ordination about the platinum atom departs significantly from a planar arrangement as indicated by the dihedral angle of 6.3° between the planes Pt,As(1),As(2) and Pt,C(1),C(2).

A common feature of transition-metal-olefin complexes of this type is the loss of planarity of the atoms about the olefinic-bond upon co-ordination. An important structural parameter is the dihedral angle between the planes defined by the co-ordinated olefin carbon atoms and their substituents (Stalick and Ibers, 1970). For a planar olefin this angle (α) is, of course, zero. The value of α in this structure, for the planes defined by C(1),F(1),F(2) and C(2),F(3),C(3) is 86°. The nature of the out of plane distortion can be seen in Figure 3.1. This view, which is approximately normal to the Pt,C(1),C(2) ring, shows the bending back of the substituents at C(1) and C(2) away from the platinum atom. The non-bonded distances of the platinum atom from these substituents range from 2.86 to 3.17Å. Large values of α for co-ordinated fluoro-olefins have been observed elsewhere (e.g. Guggenberger and Cramer, 1972; Browning and Penfold, 1973; Baraban and McGinnety, 1974; Russell and Tucker, 1975).

The environment of the other, unco-ordinated, olefin bond (C(3)-C(4)) is close to planar with the angle for the dihedral angle between the planes C(3),C(2),F(4) and C(4),F(5),F(6) being 7°.

Perspective views of the triphenylarsine ligands are shown in Figures 3.2a and 3.2b. The important intramolecular

Table 3.8

Least-squares Planes of $(AsPh_3)_2\overline{PtCF_2CFCFCF_2}$

(i) Atoms defining planes

plane(1)	plane(2)	plane(3)	plane(4)	plane(5)	plane(6)
Pt	Pt	C(1)	C(2)	C(2)	C(4)
As(1)	C(1)	F(1)	C(3)	C(3)	F(5)
As(2)	C(2)	F(2)	F(3)	F(4)	F(6)

(ii) Distances of selected other atoms from planes (Å)

	plane(1)	plane(2)	plane(3)	plane(4)	plane(5)	plane(6)
Pt	-	-	-1.090(2)	0.226(2)	-0.944(2)	-1.350(2)
As(1)	-	0.100(3)	-1.389(3)	2.603(3)	0.543(3)	-0.081(3)
As(2)	-	0.223(3)	-3.388(3)	-0.671(3)	-2.731(3)	-3.121(3)
C(1)	0.16(4)	-	-	-1.33(4)	-1.37(5)	-1.61(5)
C(2)	0.22(5)	-	0.85(5)	-	-	-0.32(5)
C(3)	-0.80(7)	-1.14(7)	1.89(7)	-	-	-0.37(6)
C(4)	-1.11(9)	-1.40(9)	1.77(8)	1.02(9)	0.48(8)	-
F(1)	1.20(2)	1.02(2)	-	-2.27(2)	-1.49(3)	-1.55(3)
F(2)	-0.95(2)	-1.13(2)	-	-1.96(2)	-2.39(3)	-2.65(3)
F(3)	1.55(2)	1.27(2)	1.53(2)	-	1.04(2)	0.84(2)
F(4)	-0.94(4)	-1.40(4)	2.87(5)	-0.62(4)	-	-0.30(5)
F(5)	-1.69(3)	-1.90(3)	1.22(3)	2.09(3)	0.63(3)	-
F(6)	-2.45(4)	-2.86(4)	2.87(4)	1.37(4)	0.58(3)	-

(iii) Interplanar angles (°)

1-2	6.3	2-3	92.4	2-4	96.3	2-5	65.1
2-6	59.8	3-4	85.6	3-5	53.5	3-6	51.7
4-5	48.6	4-6	53.5	5-6	7.2		

contacts (less than 3.4Å) involving atoms not bonded to a common atom are marked. The arsenic atoms in each ligand lie within 0.05-0.18Å from the planes of the phenyl rings.

A common geometry for triphenylphosphine and triphenylarsine ligands, as well as that of triphenylphosphorous (Daly, 1964) is the propeller conformation. In a metallo-complex with triphenylarsine ligands in such a conformation, the β-carbon* atoms corresponding to the smaller As....C(β) contacts are on the same side of the mean As,C(α),C'(α),C"(α) plane of the ligand as the metal atom (Russell and Tucker, 1975). This is because the As-C(α)-C(β) angles involving the β-carbon atom above the As,C,C',C" plane are larger than those involving the β-carbon atoms below it, thus minimising non-bonded contacts between the phenyl rings.

In this molecule one triphenylarsine ligand has a true propeller conformation (Figure 3.2b) but in the other ligand (Figure 3.2a) Ring(2) is twisted slightly away from such a conformation. The two propellers are of opposite chirality. Both β-carbon atoms of Ring(2) are on the opposite sides of the mean As(1),C(1α),C(2α),C(3α) plane as the platinum atom. This twisting is probably necessary to relieve the intramolecular contracts between Ring(2) and Ring(6). There is a close contact of 3.44Å between one β-carbon of Ring(6) and a β-carbon of Ring(2) and another of 3.34Å between the other β-carbon of Ring(6) and a β-carbon of Ring(3). (The

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* The α-carbon atoms in the phenyl rings are those directly bonded to the arsenic atoms.

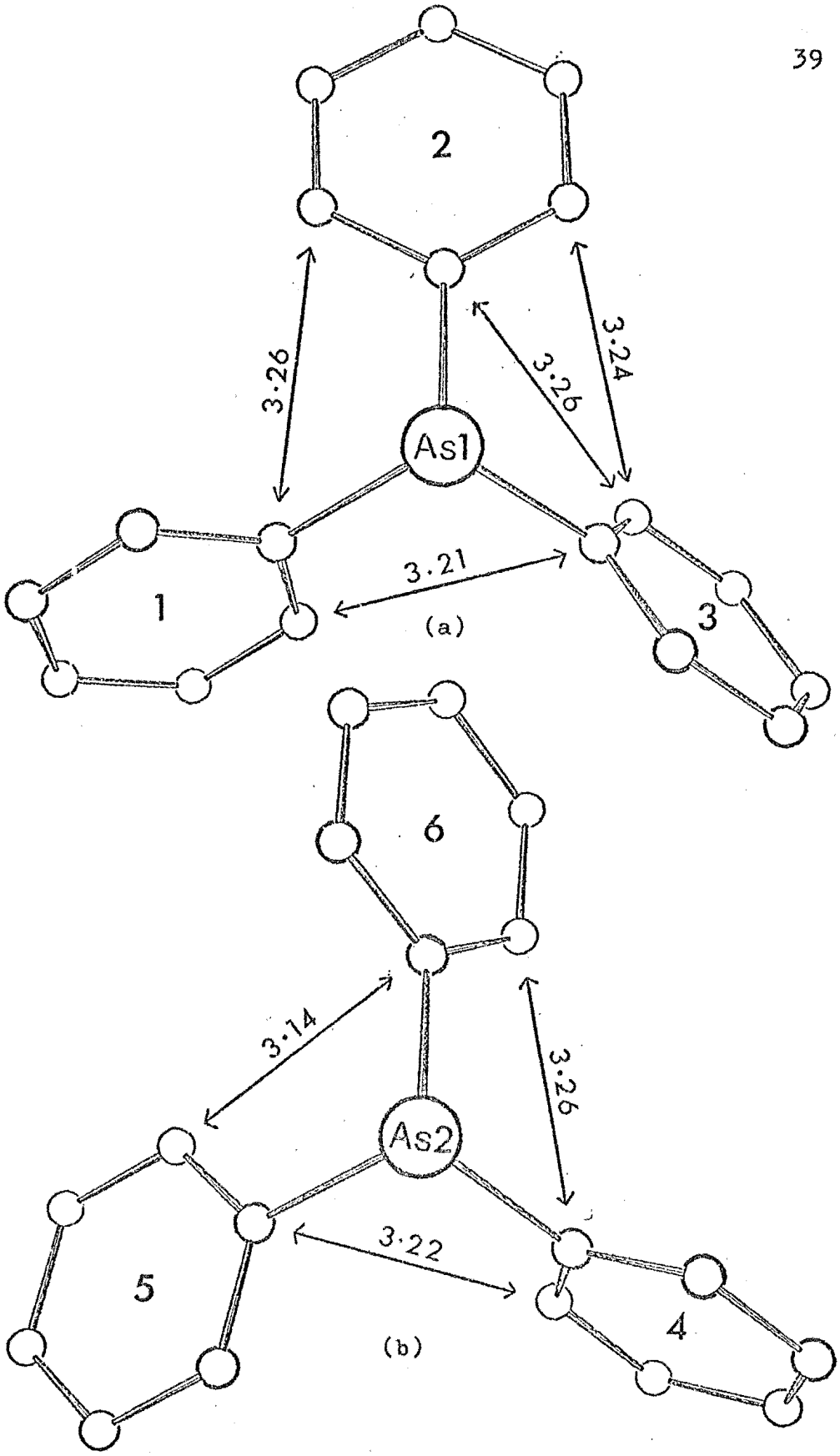


Figure 3.2

Conformations of the triphenylarsine ligands

(a) Ligand (1) viewed down the Pt-As(1) bond.

(b) Ligand (2) viewed down the Pt-As(2) bond.

Van der Waal's thickness of an aromatic ring is 3.4Å (Pauling, 1960).) The angle between the planes of Ring(2) and Ring(6) is 43° and that of those of Ring(3) and Ring(6) is 41°. There are also fairly short intramolecular contacts between F(5) and the α-carbon of Ring(1) and F(5) and one β-carbon of Ring(3) (3.17 and 3.19Å respectively). The other short intramolecular contact of atoms not bonded to a common atom is As(1)....F(5) (3.36Å).

The molecules are well separated with the closest approach being between phenyl-carbon ring atoms and fluorine atoms. There are six such contacts in the range 3.1-3.4Å.

3.5 DISCUSSION

This analysis has confirmed that there are two isomers of bis(triphenylarsine)hexafluorobuta-1,3-diene platinum. The dominant reaction product has the expected structure with the butadiene ligand co-ordinated to form a 'metallo-cyclopropane' ring. The other isomer, shown in Figure 3.3, has a 'metallo-cyclopentene' structure. Both isomers are included in Table 3.9 ((VIIa) and (VIIb)) which compares structural parameters of eight olefin complexes of platinum. All but (VIIb) have structures containing a Pt,C,C ring. (VIIb) is close to square-planar, in spite of the 6° angle between the normals of planes C(1),Pt,C(2) and As(1),Pt,As(2), and the conformation of C(1) and C(2) is better described as tetrahedral rather than trigonal.

The main features of (I) to (VIIa) in Table 3.9 agree well, especially the fluoro-olefin complexes (V)-(VIIa). There is similar geometry about the platinum atoms in all,

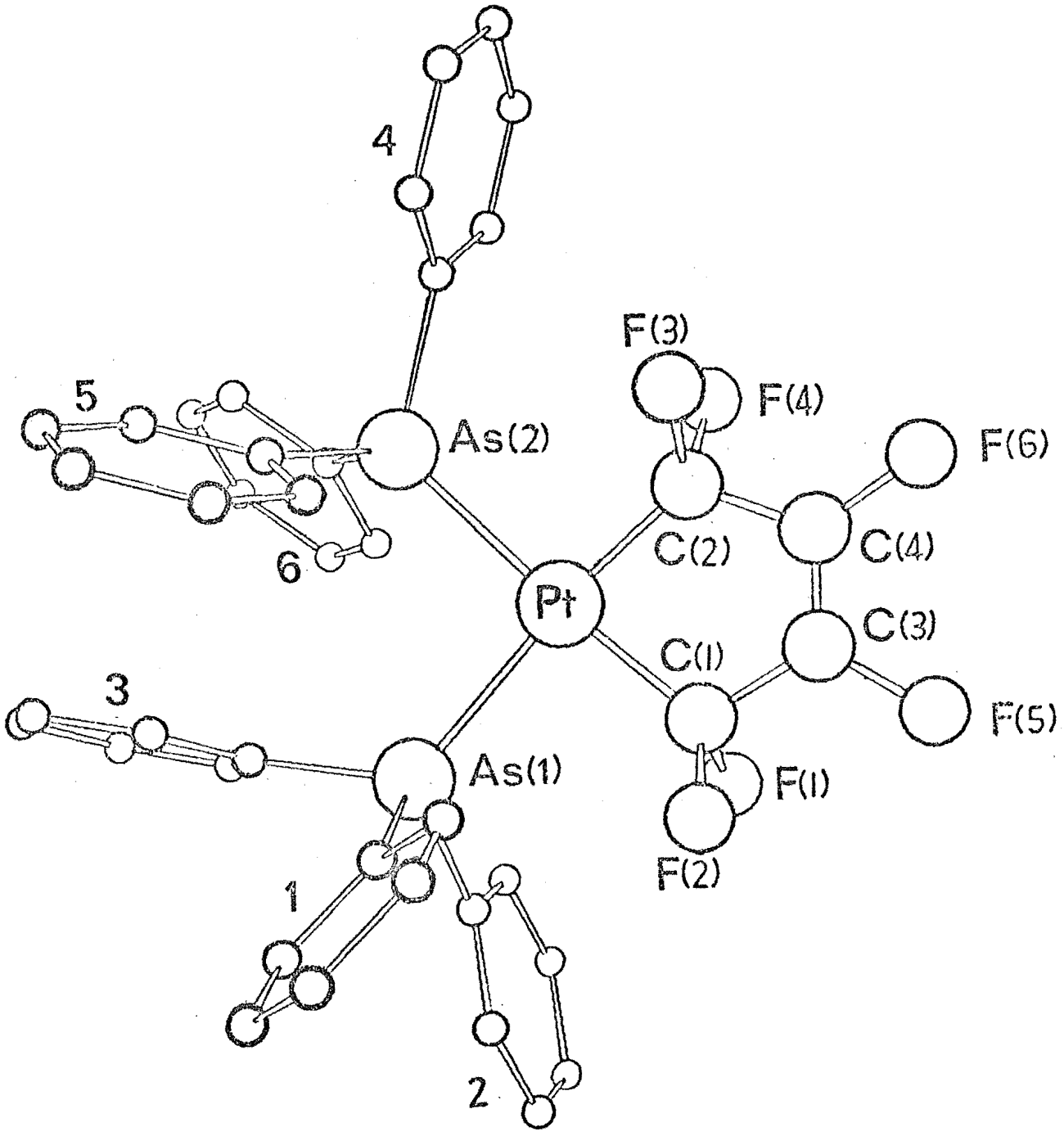


Figure 3.3

A perspective view of one molecule of

$(AsPh_3)_2\overline{PtCF_2CFCFCF_2}$

Table 3.9

Comparison of the Geometries of Some Complexes $(Ph_3L)_2Pt(olefin)$, (L = As or P)

olefin	L	Pt-C(1)	Pt-C(2)	C(1)-C(2)	L-Pt-L
(I) $(CN)_2C=C(CN)_2$	P	2.12(3)	2.10(3)	1.49(5)	101.4(3)
(II) $Cl_2C=CCL_2$	P	2.02(3)	2.05(3)	1.62(3)	100.6(2)
(III) $Cl_2C=C(CN)_2$	P	2.00(3)	2.10(2)	1.42(5)	102.0(2)
(X(1)=X(2)=Cl, X(3)=X(4)=CN)					
(IV) $H_2C=CH_2$	P	2.106(8)	2.116(9)	1.43(1)	110.5(2)
(V) $F_2C=CF_2$	As	1.99(1)	2.04(1)	1.45(2)	103.7(1)
(VI) $(CF_3)FC=CF(CF_3)$	P	2.03(1)	2.05(1)	1.43(1)	105.9(1)
(VII) $F_2C=CF(CFCF_2)$	As				
(a) (X(1)=X(2)=X(3)=F, X(4)=C)		1.97(4)	1.98(5)	1.54(5)	100.1(1)
(b) (X(1)=X(2)=X(3)=X(4)=F)		1.97(3)	1.89(4)	-	94.5(1)

Table 3.9 contd.

olefin	C(1)-Pt-C(2)	X(1)-C(1)-X(2)	X(3)-C(2)-X(4)	dihedral angle L,Pt,L/C(1),Pt,C(2)
(I) $(CN)_2C=C(CN)_2$	42(1)	110(4)	116(3)	8.3
(II) $Cl_2C=CCL_2$	47(1)	116(2)	106(2)	12.3
(III) $Cl_2C=C(CN)_2$	40.6(9)	110(1)	114(2)	1.9
(X(1)=X(2)=Cl,X(3)=X(4)=CN)				
(IV) $H_2C=CH_2$	42.1(5)	-	-	1.6
(V) $F_2C=CF_2$	42.1(5)	107.2(9)	107.4(10)	0
(VI) $(CF_3)FC=CF(CF_3)$	41.0(4)	105(1)	104(1)	10.8
(VII) $F_2C=CF(CFCF_2)$				
(a) (X(1)=X(2)-X(3)=F,X(4)=C)	46(1)	107(3)	110(4)	6.3
(b) (X(1)=X(2)=X(3)=X(4)=F)	82(2)	99(2)	96(3)	6.0

References

(I) (Bombieri et al., 1970)

(II) (Francis, McAdam and Ibers, 1971)

(III) (McAdam, Francis and Ibers, 1971)

(IV) (Cheung and Nyburg, 1972)

(V) (Russell and Tucker, 1975)

(VII) (Baraban and McGinnety, 1975)

(VIIa) This work

(VIIb) (Holloway, 1973)

although the dihedral angles between the planes C(1),Pt,C(2) and L(1),Pt,L(2) vary from 0 to 12°. In all the complexes the C(1)-C(2) bond is longer than the corresponding bond in the free olefin (e.g. 1.31(4) for C_2F_4 (Karle and Karle, 1950)). Further, the olefins in all cases have lost planarity upon co-ordination. A problem with analyses of this kind is the high standard deviations of the bond distances and angles; a consequence of the overwhelming diffracting power of the heavy atom.

While many models for the bonding of olefins to transition metals have been proposed, the generally accepted model (Ittel and Ibers, 1976) for complexes containing three-membered M,C,C rings, is based on the proposals of Dewar (1951) and Chatt and Duncanson (1953). These consider the π-donor and π-acceptor properties of the ligand rather than considering the bonding as two separate metal-carbon σ bonds as suggested by the term 'metallo-cyclopropane'. In terms of this model, the metal atom in complexes of the type $(Ph_3L)_2M(olefin)$ (L=As or P) is regarded as three co-ordinate rather than four co-ordinate and the complexes are described as being approximately 'trigonal-planar' (Figure 3.4). The bonding

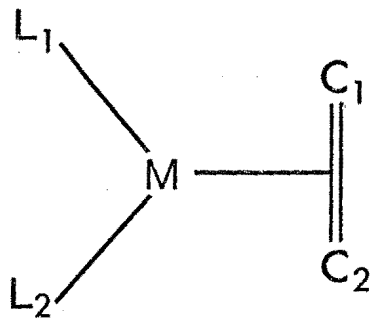


Figure 3.4 Three co-ordinate trigonal planar olefin complex. The five atoms are coplanar.

may be described as involving formation of a σ-bond by donation of π-electrons to the metal atom and formation of a π-bond by back donation from the d-orbitals of the metal atom to the olefin π*-orbital. The nature of the metal-olefin interaction can be viewed as a competition between the metal-π and metal-π* interaction (de Boer and Bright, 1975). If the former is predominant then the conformation of the olefin will be identical with that of the free molecule. However if the latter is more important then the olefinic bond should be longer and the conformation closer to tetrahedral than in the free ligand. Unfortunately this model has been shown to be inadequate when used to explain details in the observed geometries in a range of metal-olefin complexes. A recent review by Ittel and Ibers (1976) discusses these inadequacies and outlines alternative models which have been proposed to describe the redistribution of electrons resulting from co-ordinating unsaturated molecules to transition metal atoms.

It is evident, from the large thermal parameters and large standard deviations, that the unco-ordinated olefin function $-CF=CF_2$ in this complex, is not well characterised structurally. Similar problems have been experienced in the analyses of $(Ph_3P)_2\overline{PtCCl_2CF_2}$ (Francis, McAdam and Ibers, 1971) and $(Ph_3P)_2Pt(CCH_3)_2CH_2$ (de Boer and Bright, 1975). The C(3)-C(4) distance (1.25(7)Å) is significantly shorter, than expected. The normal range of C-F bonds is 1.30-1.38Å (Sutton, 1958; 1965). Similarly, the angles C(2)-C(3)-C(4) at 89(8)°, F(5)-C(4)-C(3) at 158(9)° and F(5)-C(4)-F(6) at 84(5)° differ significantly from what is

usually observed. Because of the large errors in atom positions we can attach no chemical significance to these differences. Although the hexafluorobutadiene ligand of the molecule is not as well characterised as is desirable, the geometry about the platinum atom has been established unequivocably. Furthermore the molecule has been shown to have the structure originally proposed by Maples et al. (1974).

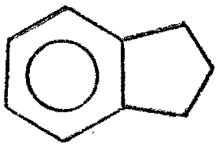
CHAPTER 4

STRUCTURAL STUDY OF 1,1-DICHLORO-2,5-DIPHENYLCYCLOPROPABENZENE

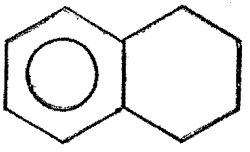
4.1 INTRODUCTION

Cyclopropabenzene, formed by the fusion of cyclopropene to a benzene ring, is the most highly strained member of the cycloalkabenzene series. A most interesting facet of the chemistry of these compounds, is the expectation of partial localisation of the π-electron framework with consequent bond length alternation in the aromatic ring (Halton, 1973).

As early as 1930 the differences in the reactivities of indan(VIII) and tetralin(IX) were explained in terms of

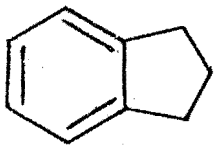


(VIII)

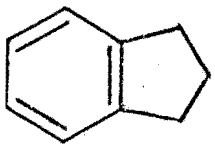


(IX)

aromatic bond localisation in the direction shown in (Xa) (Mills and Nixon, 1930). Theoretical studies of bond length and bond angle strain in indan (Longuet-Higgins and Coulson, 1946) led to the conclusion that (Xb) would be more favourable. Similar bond length and bond angle variations would



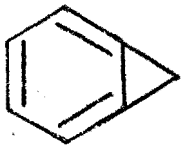
(Xa)



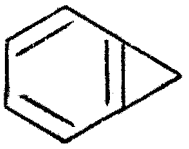
(Xb)

be expected in the more highly strained cycloalkabenzenes including cyclopropabenzene. X-ray structure determinations of cyclobutabenzene derivatives (Hardgrove, Templeton and Templeton, 1968; Lawrence and MacDonald, 1969; Allen and Trotter, 1970a, 1970b), appeared to be reasonably consistent with the Longuet-Higgins-Coulson predictions.

Subsequent CNDO/2 semi-empirical molecular orbital calculations (Cheung, Cooper and Manatt, 1971) predicted geometry with bond localisation throughout the cycloalkabenzene series in the opposite direction to Longuet-Higgins and Coulson, i.e. for cyclopropabenzene in the direction (XIa) rather than (XIb). The bond distances and bond angles for cyclopropabenzene, from these calculations, are given in Figure 4.1. The directions of bond angle changes from 120° in the benzene ring agree in both sets of molecular orbital calculations.



(XIa)



(XIb)

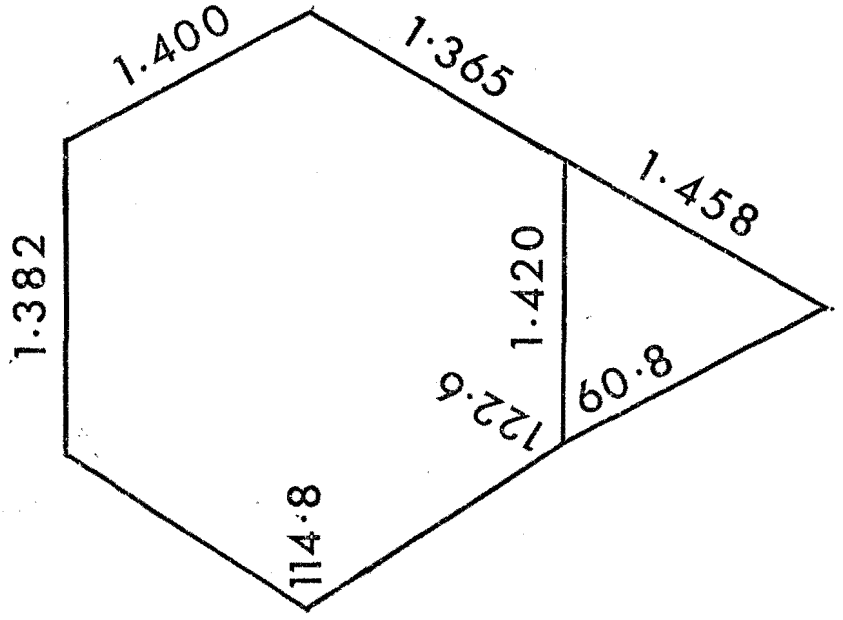


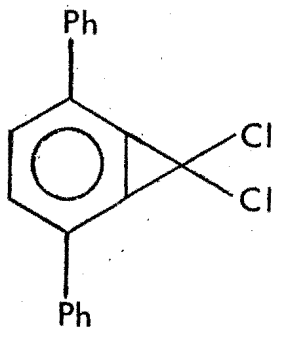
Figure 4.1

CNDO/2 Calculated Geometry for Cyclopropabenzene

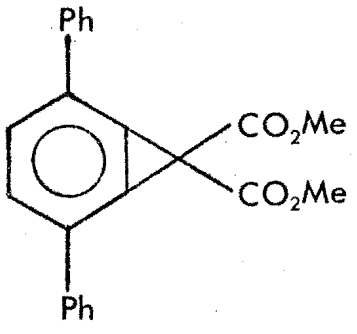
In 1964, the first substantiated report of a successful synthesis of a cyclopropabenzene derivative appeared in the literature (Anet and Anet, 1964). By the late 1960's a number of derivatives had been reported. Preparative and reaction chemistry of these compounds have been described in the review article by Halton (1973).

From nmr studies ((Vogel, Korte, Grimme and Günther, 1968a, 1968b), (Cooper and Manatt, 1970), (Pawlizek and Günther, 1971) and (Günther and Pawlizek, 1971)), it was inferred that cyclopropabenzene was nearly planar, with bond angle deformations similar to those predicted by the theoretical calculations. These studies did not, however, establish any bond localisation.

Thus by 1971, there was a need for an accurate crystal structure analysis of a cyclopropabenzene derivative in order to characterize any bond localisation. Crystals of 1,1-dichloro-2,5-diphenylcyclopropabenzene (Halton and Milsom, 1971) (XII) suitable for X-ray studies, were used to establish the space group as $P2_12_12_1$. Diffraction data, collected in July 1971, were used in several unsuccessful attempts to determine the crystal structure from its Patterson synthesis.



(XII)



(XIII)

Eventually, three years later, the crystal structure was solved. Some of the initial interest in the problem had been lost, in the meantime, because of the publication of the crystal structure of dimethyl 2,5-diphenylcyclopropabenzene-1,1-dicarboxylate (XIII) (Carstensen-Oeser, Müller and Dürr, 1972). From a crystallographic point of view however, interest in (XII) had increased because of its resistance to solution by routine structural solving techniques. The steps taken in the determination of the structure of (XII) and the outcome are described in this chapter. This structure has also been published in 'Acta Crystallographica' (Halton, McLennan and Robinson, 1976).

4.2 EXPERIMENTAL

Colourless crystals suitable for X-ray diffraction experiments were supplied by Dr. Brian Halton of Victoria University of Wellington. The method of preparation used was the treatment of 1,5-diphenylcycloheptene with tert-butoxide in tetrahydrofuran (Halton and Milsom, 1971).

Weissenberg and precession photographs showed conditions limiting reflections uniquely consistent with space group $P2_12_12_1$ (h00, h=2n; 0k0, k=2n; and 00l, l=2n). The relevant crystal data are summarised in Table 4.1.

The intensity data were collected using nickel-filtered CuKα X-radiation, using the techniques outlined in Chapter 2. The parameters of the experiment are given in Table 4.2. As there were no systematic changes observed in the intensities of the three standard reflections

Table 4.1

Crystal Data for $C_6H_2(CCl_2)Ph_2$

Formula	$C_{19}H_{12}Cl_2$
Formula weight	311.21
System	Orthorhombic
Space group	$P2_12_12_1$
a	12.2605(5)Å
b	17.0255(9)Å
c	7.3649(6)Å
V	1537.36Å^2
D_{Calc}	1.34g cm^{-3}
Z	4
F(0,0,0)	640
μ(CuKα)	36.87 cm^{-1}

Table 4.2

Experimental Parameters for $C_6H_2(CCl_2)Ph_2$

Crystal dimensions	0.625 x 0.275 x 0.163 mm^3
Mosaicity	0.10-0.14°
θ scan range	0.72°
Scan time	72 sec.
Total background time	36 sec.
θ limit	50°
Total independent reflections	900
Reflections used in refinements for which $F_o^2 \geq 3\ (F_o^2)$	745
Weighting parameter p	0.050
Ratio of observations to parameters	3.9

monitored throughout the data collection, corrections for crystal decomposition were not included in the data reduction process. The intensities were, however, corrected for absorption using program ABSORB. Correction factors ranged from 2.1 to 2.8.

4.3 SOLUTION AND REFINEMENT OF THE STRUCTURE

The initial attempts to solve this structure involved analyses of the Patterson function. The dominant feature of this map is the set of peaks of the form (0,v,0) where v corresponds to distances from the origin at approximate multiples of 2, 3, 4 and 6 times normal carbon-carbon bond lengths. These were deduced, correctly, to be peaks from overlapped intramolecular carbon-carbon vectors. The intramolecular chlorine-chlorine vector (the sixth highest peak) perpendicular to that set, was identified along with some of the Harker vectors corresponding to the chlorine atom positions. After a number of trial chlorine atom positions gave R-factors in the region of 0.55 this approach was abandoned. It is interesting to note that a structure factor calculation including only the two chlorine atoms used in the actual refinements at their refined positions gave

$$R_1 = 0.579 \quad \text{and}$$

$$R_2 = 0.695.$$

The approach that eventually led to the correct structure was the use of direct methods. This was the first structure solved in this laboratory using program

MULTAN. The successful program execution used 154 normalised structure factors to generate 2000 triplets. The starting set for the tangent refinement procedure consisted of those |E|'s needed to fix the origin and the enantiomorph, the |E| corresponding to the most intense reflection with its phase set at 0, and three further |E|'s. The eight phase sets so generated had the 'figures of merit' (Section 2.2.2) of Table 4.3. The MULTAN program manual (Main, et al., 1971, page 15) suggests 'that it is very unlikely that correct phases would make ABS FOM (the absolute figure of merit) as low as 0.80'. Thus it was pleasing when a Fourier synthesis of the phased normalised structure factors of set 4 led to the correct structure.

A planar molecule, such as the one described here, is not the arrangement of atoms that direct methods work most satisfactorily for. In this case the mean values of $|E|^2$ for the eight different parity groups ranged from 0.75 (for e.oe) to 1.43 (ee.o). As a direct consequence some of the stringent requirements in the routines used by MULTAN to find suitable reflections for origin definition had to be relaxed in this case. The program SHNORM which was used to generate the normalised structure factors did not have the feature of its replacement program NORMAL (Chapter 8). From subsequent experience with the MULTAN74 program package, of which NORMAL is a part, it would seem that applying individual scale factors would have improved the quality of the phase sets produced.

The third highest peak of the E-map corresponded to a chlorine atom position and co-ordinates for 17 out of the

Table 4.3

'Figures of Merit'

for $C_6H_2(CCl_2)Ph_2$

Phase set no.	absolute figure of merit	residual
1	0.667	0.37
2	0.673	0.33
3	0.760	0.30
4	0.773	0.32
5	0.730	0.34
6	0.668	0.33
7	0.755	0.31
8	0.766	0.31

19 carbon atoms were extracted from the lower peaks. The two highest peaks showed up inadequacies in the phasing in that they corresponded to the centres of the terminal phenyl rings. From these established carbon atom positions it was possible to calculate co-ordinates for those atoms missing from regular hexagonal phenyl groups. Thus the first structure factor calculation included one chlorine atom, and seven carbon atoms in addition to two calculated phenyl rings treated as rigid bodies. Values obtained from this calculation were

$$R_1 = 0.440 \quad \text{and}$$
$$R_2 = 0.578.$$

This was not particularly encouraging, with just one atom missing, in view of the figure quoted for a random arrangement of atoms in a non-centric space group (0.59) (Wilson, 1950). The missing chlorine position corresponded to the highest peak in a first difference Fourier synthesis. This model, including all non-hydrogen atoms but still treating the terminal phenyl rings as regular hexagons, after two cycles of refinement gave

$$R_1 = 0.297 \quad \text{and}$$
$$R_2 = 0.391.$$

The model obtained by removing the constraints on the terminal phenyl rings and describing all atoms by isotropic thermal parameters converged at

$$R_1 = 0.270 \quad \text{and}$$
$$R_2 = 0.352.$$

A possible explanation for the unexpected absence of the second chlorine atom from the original F_o Fourier map appeared at this stage. This atom had an isotropic temperature factor twice that of the other chlorine atom and it was also higher than those of all the other atoms in the molecule.

The next step in the refinement procedure proved too ambitious. All atoms were refined with anisotropic thermal parameters. After several cycles the temperature factors were still non-positive definite for five atoms. An explanation for the problems being experienced with the refinements that was examined at this time, was the possibility that the molecule was not correctly placed in the cell. After exploring other possibilities it was decided to re-investigate the earlier model.

A model with anisotropic thermal parameters for only the chlorine atoms was refined. After an unexpectedly large number of cycles, with quite large shifts in some carbon positions, this model converged at

$$R_1 = 0.100 \quad \text{and}$$
$$R_2 = 0.140.$$

From a difference Fourier synthesis it was then possible to establish the approximate positions of the twelve hydrogen atoms. (Carbon-hydrogen distances ranged from 0.84-1.27Å and the hydrogen-carbon-carbon angles from 107°-109°). The final refinements, in two large blocks, incorporated the hydrogen atoms at fixed, calculated positions* with fixed

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* C-H bond distances were set at 0.95Å (Churchill, 1973).

temperature factors of 0.063. All the non-hydrogen atoms were given aniosotropic thermal parameters. After each pair of refinements new hydrogen atom positions were calculated from the refined carbon positions, until these refinements converged with

$$R_1 = 0.077 \quad \text{and}$$
$$R_2 = 0.112.$$

In the final stages, after an examination of structure factors had shown twelve low angle and intense structure factors with evidence of extinction, an extinction parameter was also refined (Zachariasen, 1963, 1967). The final value of this parameter was $8(3) \times 10^{-8}$. Final values obtained were

$$0.060 \text{ for } R_1 \quad \text{and}$$
$$0.088 \text{ for } R_2.$$

A structure factor calculation for all 900 reflections gave

$$R_1 = 0.073 \quad \text{and}$$
$$R_2 = 0.091.$$

These structure factors are listed in Appendix 3. In the final cycle the largest positional shift was 0.14σ and the average shift was 0.05σ. The standard error in an observation of unit weight was 2.9. A final difference Fourier synthesis showed no peaks greater than the heights of the peaks of the hydrogen atoms located earlier.

The final positional and thermal parameters for the non-hydrogen atoms are given in Table 4.4 and the positional

Table 4.4

Positional ($\times 10^4$) and Thermal Parameters ($\times 10^3$) for the Non-hydrogen Atoms of $C_6H_2(CCl_2)Ph_2$

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl(1)	72(5)	146(2)	3303(6)	309(7)	80(2)	132(3)	-8(3)	135(4)	-6(2)
Cl(2)	-1639(2)	36(2)	556(11)	74(2)	81(2)	53(1)*	-6(2)	95(4)	-49(5)
C(11)	1138(9)	1028(6)	-1343(16)	63(8)	85(8)	48(8)	0(7)	1(6)	2(6)
C(12)	457(8)	526(6)	-313(17)	49(7)	73(7)	86(9)	9(6)	2(7)	6(7)
C(13)	524(8)	-266(6)	-347(16)	66(7)	69(7)	74(7)	-2(5)	15(7)	-1(6)
C(14)	1262(9)	-725(6)	-1297(15)	68(8)	74(7)	54(8)	7(6)	-7(7)	-6(6)
C(15)	1891(11)	-231(7)	-2406(16)	105(9)	82(9)	86(9)	16(7)	33(8)	-0(7)
C(16)	1845(10)	583(7)	-2388(15)	96(9)	86(8)	59(8)	-5(7)	34(7)	4(6)
C(21)	1336(10)	-1579(6)	-1151(14)	75(8)	68(7)	33(8)	6(7)	-5(6)	-6(5)
C(22)	556(9)	-1996(6)	-217(17)	81(8)	69(7)	72(9)	14(6)	5(8)	-4(6)
C(23)	582(9)	-2802(7)	-65(18)	84(8)	78(8)	83(9)	8(7)	9(8)	-5(7)
C(24)	1432(12)	-3202(6)	-877(18)	97(9)	65(7)	10(1)*	11(7)	9(9)	-11(7)
C(25)	2215(10)	-2803(8)	-1797(21)	77(9)	10(1)*	10(1)*	33(8)	3(8)	-9(9)
C(26)	2171(10)	-1998(7)	-1927(17)	9(1)*	78(8)	74(9)	15(7)	12(8)	-3(7)

Table 4.4 contd.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(31)	1048(12)	3505(6)	-826(17)	10(1)*	74(7)	57(8)	-13(8)	0(8)	-8(6)
C(32)	247(10)	3058(6)	-27(16)	11(1)*	72(7)	64(8)	-3(7)	13(8)	-11(6)
C(33)	291(8)	2247(6)	-204(14)	81(8)	70(7)	50(7)	-16(6)	-3(7)	13(6)
C(34)	1121(10)	1896(6)	-1221(14)	73(8)	64(7)	52(9)	-1(6)	-13(7)	-4(6)
C(35)	1916(9)	2358(7)	-1991(15)	85(8)	79(8)	61(8)	-24(7)	20(7)	-7(7)
C(36)	1868(10)	3160(7)	-1832(17)	85(9)	89(8)	60(8)	-36(7)	12(7)	3(7)
C(40)	-250(9)	97(6)	919(20)	91(7)	63(6)	16(1)*	-8(7)	50(9)	-7(9)

* These parameters are $x10^2$ not $x10^3$.

Table 4.5

Positional Parameters ($x10^3$) for the Hydrogen Atoms of $C_6H_2(CCl_2)Ph_2$

	x	y	z
H(C15)	239	-48	-323
H(C16)	234	86	-316
H(C22)	-2	-172	35
H(C23)	2	-308	57
H(C24)	147	-376	-79
H(C25)	280	-308	-235
H(C31)	103	406	-68
H(C32)	-33	330	63
H(C33)	-24	193	37
H(C35)	251	212	-263
H(C36)	239	348	-241
H(C26)	272	-173	-257

parameters for the hydrogen atoms are given in Table 4.5.

4.4 DESCRIPTION OF THE STRUCTURE

The labelling scheme used throughout the chapter is shown in Figure 4.2*. Bond distances and angles are marked on Figure 4.3. The maximum estimated standard deviations are 0.02Å and 1°. The carbon-chlorine distances have been corrected for thermal motion using the riding model (Busing and Levy, 1964). The distances before correction were 1.80(2)Å for Cl(1)-C(40) and 1.73Å for Cl(2)-C(40).

It is interesting to compare the structure of this molecule with that of the essentially planar p-terphenyl (Rietveld, Maslen and Clews, 1970). From Figure 4.4 and the analysis of least squares planes (Table 4.6) it is apparent that the cyclopropabenzene ring system is not planar. There is severe compression of the central six-membered ring with the internal angles about the carbon atoms alpha to the three-membered differing significantly from 120° (108(1) and 110(1)° about C(14) and C(11), respectively). Thus, the planes of the phenyl substituents are twisted and bent from the plane containing C(13), C(12), C(15) and C(16). The angles between the terminal planes and the approximate plane of the central benzene ring are 9.8 and 9.9° (Table 4.6). Figure 4.5 gives detailed

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* Hydrogen atoms have been omitted from the diagrams and they are numbered according to the carbon atoms to which they are attached.

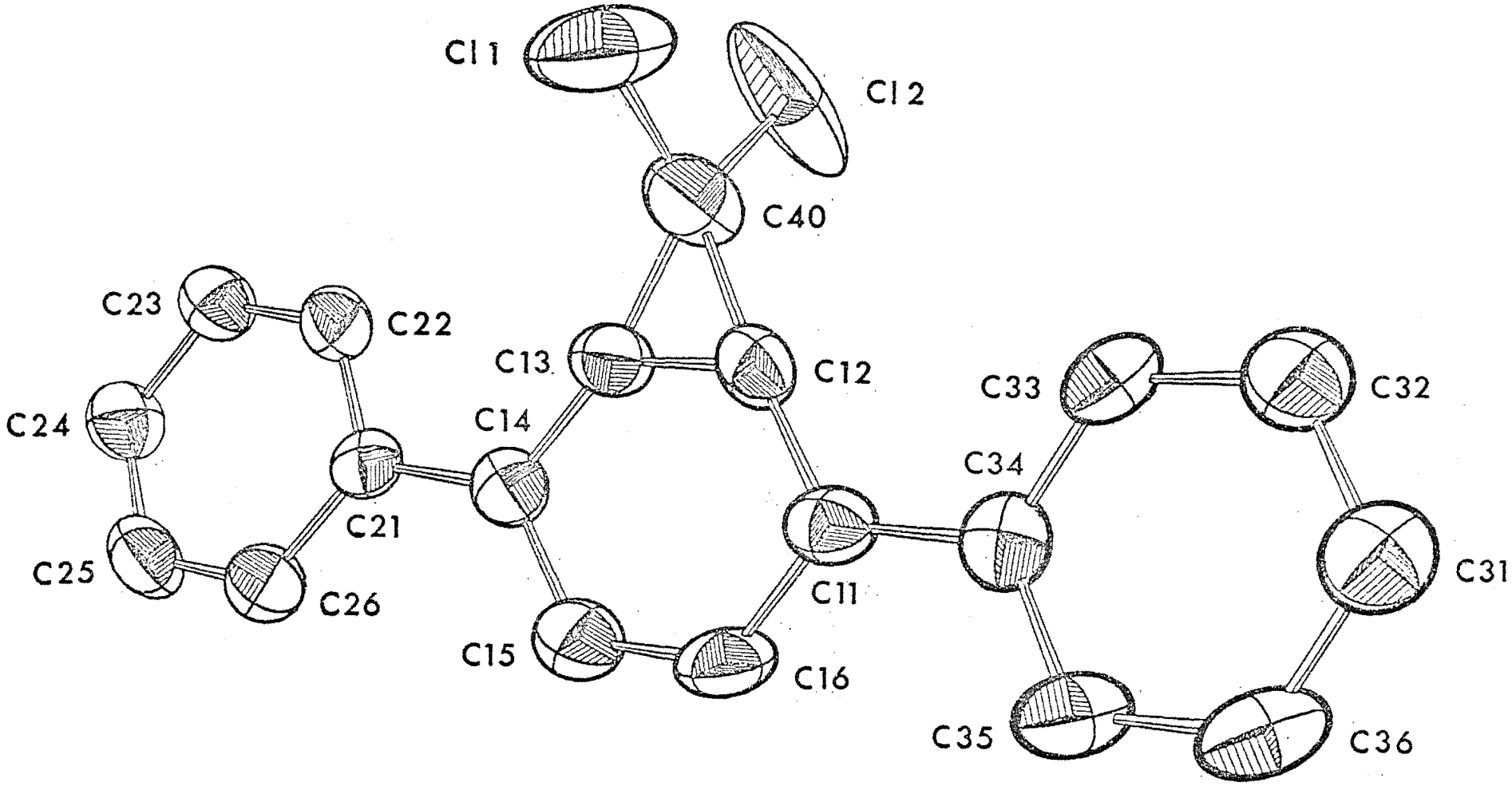
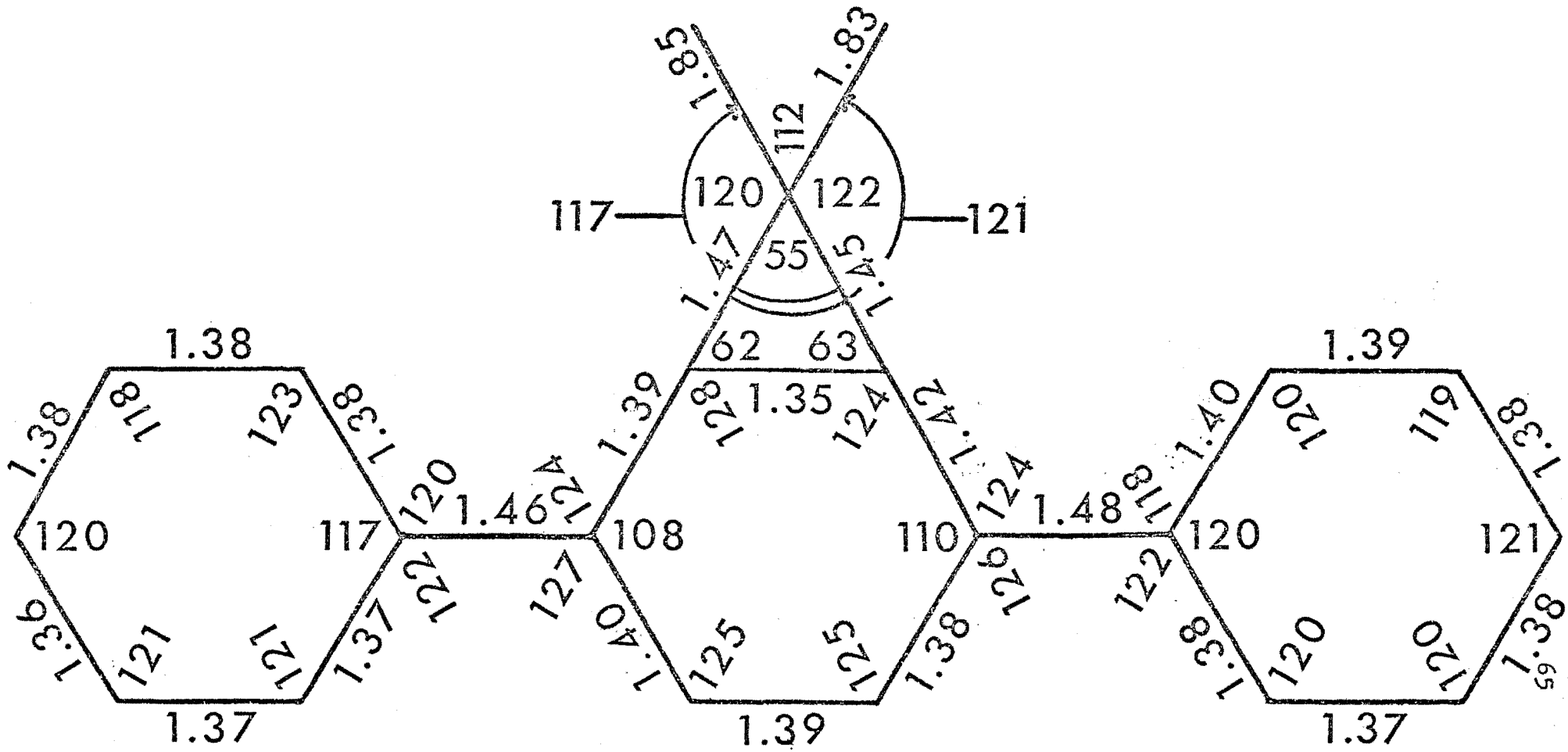


Figure 4.2

A perspective view of one molecule of $C_6H_2(CCl_2)Ph_2$

Figure 4.3

Bond distances (Å) and angles (°) in $C_6H_2(CCl_2)Ph_2$


1.85
1.83
112
120
122
117
121
55
1.47
1.45
62
63
1.35
1.38
1.39
1.42
1.46
1.48
1.40
1.39
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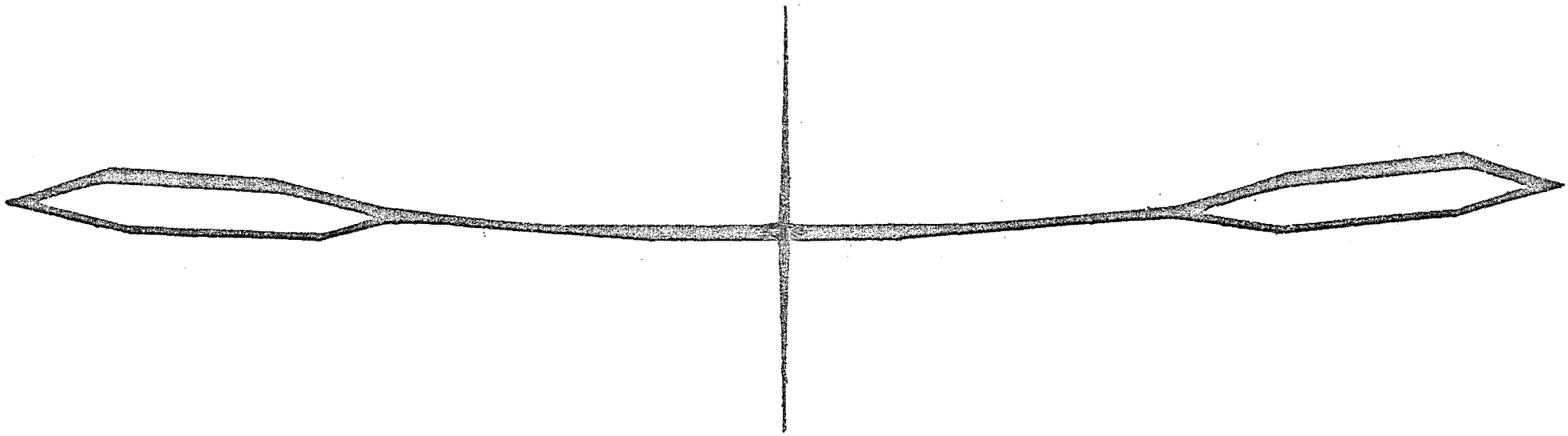


Figure 4.4

A perspective view of a molecule down the C(16)-C(12) vector

Table 4.6

Least-squares Planes of $C_6H_2(CCl_2)Ph_2$

(a) Atoms defining planes and distances of atoms from planes (Å)

Plane 1		Plane 2		Plane 3		Plane 4		Plane 5	
Cl(1)	0.0	C(12)	0.0	C(11)	-0.018	C(21)	-0.005	C(31)	-0.007
Cl(2)	0.0	C(13)	0.0	C(12)	0.007	C(22)	-0.003	C(32)	0.004
C(40)	0.0	C(40)	0.0	C(13)	0.021	C(23)	0.000	C(33)	-0.006
				C(14)	-0.035	C(24)	0.001	C(34)	0.010
				C(15)	0.025	C(25)	0.001	C(35)	-0.012
				C(16)	0.001	C(26)	-0.004	C(36)	0.011

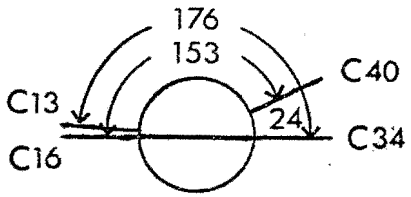
(b) Interplanar angles (°)

1 - 3	88.5	2 - 1	88.0	3 - 4	9.9	4 - 5	8.5
1 - 4	82.9	2 - 3	3.4	3 - 5	9.8		
1 - 5	81.4						

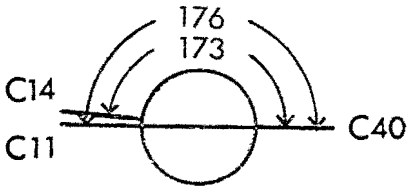
Table 4.6 contd.

(c) Distances of other carbon atoms from plane 1 (Å)

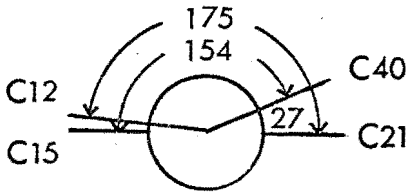
C(40)	-0.061	C(21)	-0.123	C(24)	-0.249	C(31)	-0.383	C(34)	-0.126
		C(22)	0.032	C(25)	-0.412	C(32)	-0.135	C(35)	-0.385
		C(23)	-0.022	C(26)	-0.356	C(33)	-0.024	C(36)	-0.483



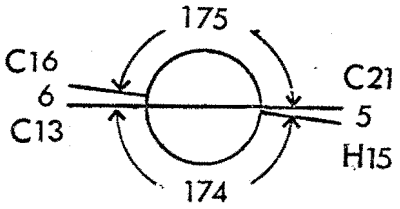
C11→C12



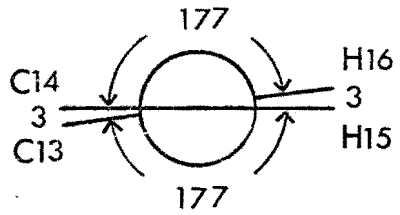
C12→C13



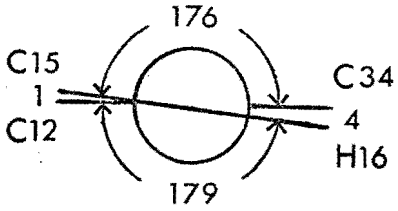
C13→C14



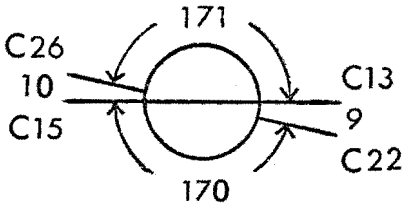
C14→C15



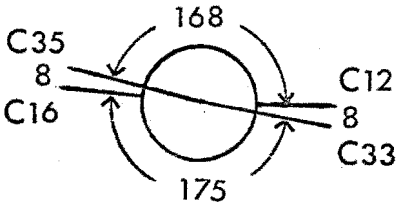
C15→C16



C16→C11



C14→C21



C34→C11

Figure 4.5

Selected torsional angles(°) in $C_6H_2(CCl_2)Ph_2$

conformational angles. The largest deviations from coplanar bond arrangements (i.e. torsional angles of 0 or 180°) occur about C(11)-C(12) and C(14)-C(13). The C(16)-C(11).... C(12)-C(40) torsional angle is 152.8°, C(34)-C(11) .... C(12)-C(40) is -24.1°, C(15)-C(14)....C(13)-C(40) is -153.9° and C(21)-C(14)....C(13)-C(40) is 26.9°. Torsional angles about the individual bonds of the phenyl substituents are not shown but the maximum deviation from planarity is 3.0° for C(34)-C(35)....C(36)-C(31).

The overall symmetry of the molecule then, rather than being C_{2v} as it would be for a completely planar molecule is close to C_s with the single mirror plane passing through atoms Cl(1), Cl(2) and C(40).

The molecules are packed with their largest dimension parallel to the long axis of the cell (Figure 4.6). From this diagram it is apparent that molecules related by screw axes parallel to the b-axis have the planes of their terminal phenyl rings parallel to each other. The bending of both terminal phenyl rings towards one chlorine atom (Cl(1)) is one consequence of the crystal packing. A further consequence is that the closest intermolecular contact is between Cl(1) and H(31) (2.88Å), where the two molecules involved are related by a screw axis parallel to the b-axis. Perhaps the difference in temperature factors of the two chlorine atoms may be attributed to this difference in packing environments. The closest intermolecular approach to Cl(2) is a Cl(2)-H(36) distance of 3.11Å.

The molecules in general are well separated and there are no contacts, other than those involving a hydrogen atom, less 3.30Å.

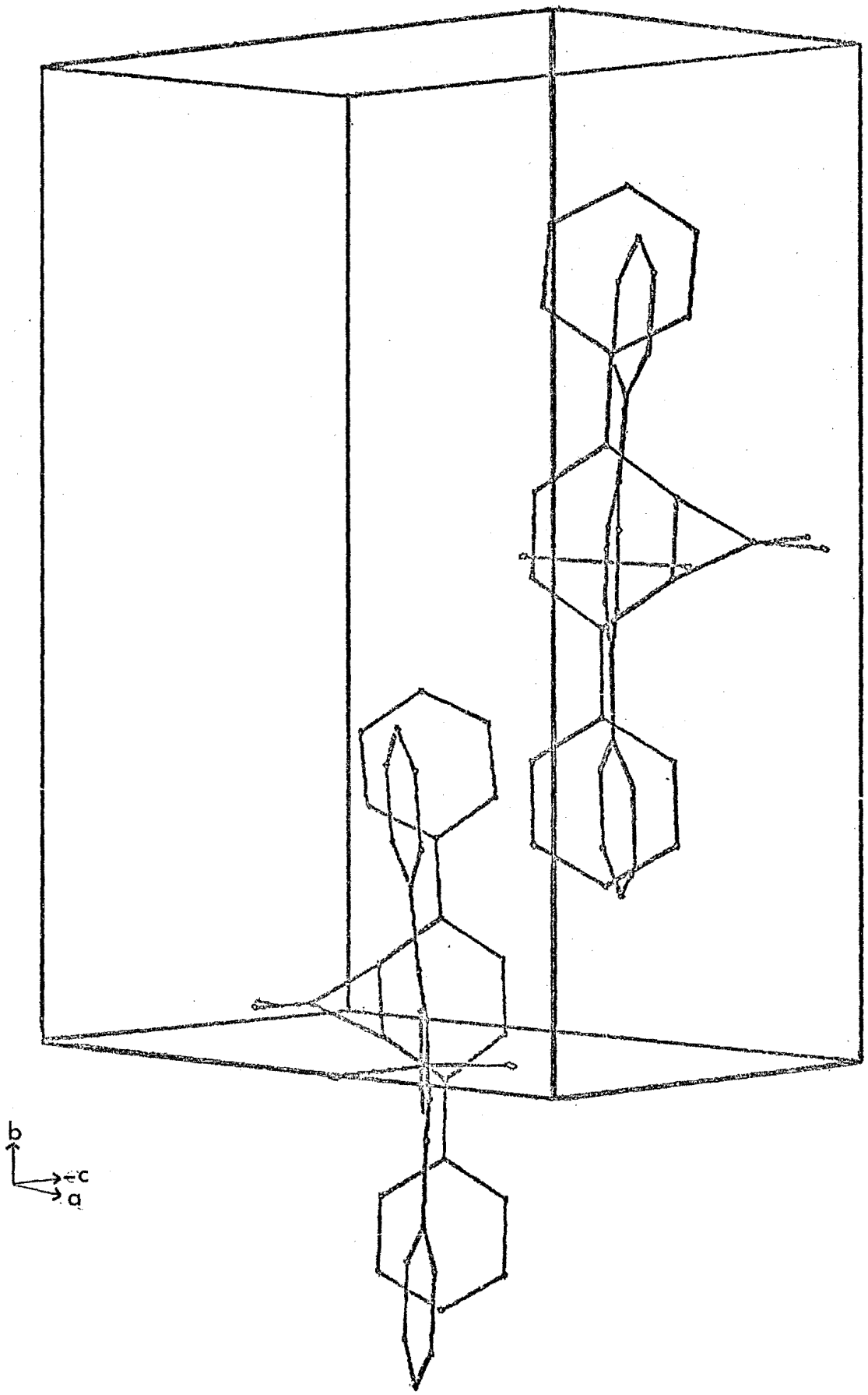
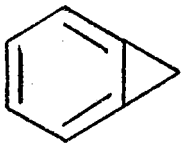


Figure 4.6

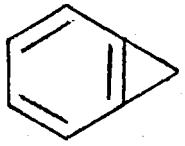
Packing of molecules of $C_6H_2(CCl_2)Ph_2$

4.5 DISCUSSION

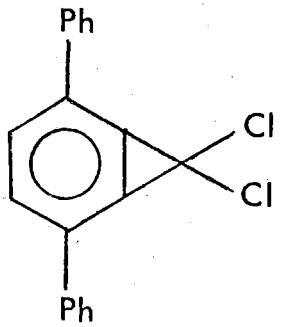
The original reason for undertaking this structure analysis was to investigate the possibility of partial localisation of the π-electron framework and a tendency towards cyclohexatriene character of the benzene ring in cyclopropabenzenes. As discussed earlier, the theoretical models which predict this localisation have failed to agree on the direction. The models are (XIb) (Longuet-Higgins and Coulson, 1946) and (XIa) (Cheung, Cooper and Manatt, 1971). The chemical properties of cyclopropabenzene are consistent with either bond localisation or severe deformation of the six-membered ring (Halton, 1973).



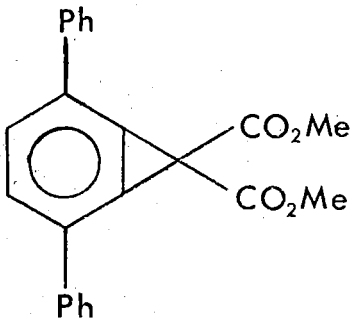
(XIa)



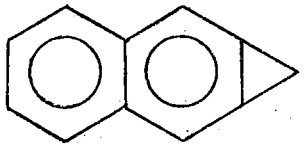
(XIb)



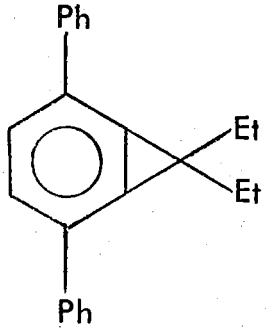
(XII)



(XIII)



(XIV)



(XV)

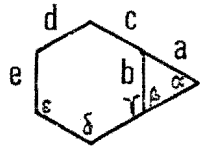
In the meantime, while difficulty was being experienced with the analysis of the dichloro-derivative (VII), there appeared in the literature reports of the structures of related compounds which crystallised in centrosymmetric space groups (dimethyl 2,5-diphenylcyclopropabenzene-1,1-dicarboxylate (XIII) (Carstensen-Oeser, Müller and Dürr, 1972) and cyclopropa(b)napthalene (XIV) (Billups, et al., 1973)). Eventually the structure of (XII) was solved. The result is not of high precision because of the limited extent of the data used in refinements. It is, however, worthwhile to compare this structure with those of other compounds containing strained cyclopropene rings. Table 4.7 lists bond distances and angles for the moleculesmentioned above and also for the structure, as yet unreported, of 1,1-diethyl-2,5-diphenylcyclopropabenzene (XV) (Müller and Dürr, 1974).

The main structural features of all four compounds agree quite well. There is no evidence, even in the more accurate of these analyses, (XIII) and (XIV), of bond localisation in either of the directions (XIa) or (XIb). The length of the bridge bond for this derivative (XII) is similar to that of (XV) and falls midway between those of (XIII) and (XIV). The ester function was suggested (Billups, et al., 1973) to be responsible for the shortened nature of the bridge bond in (XIII).

The C(40)-C(12) and C(40)-C(13) bonds ((a) in Table 4.7) are shorter at 1.45(2) and 1.47(2)Å, respectively, in this compound than in the other cyclopropa- compounds tabulated. They are, however, similar to the carbon-carbon bonds adjacent to the bridge bond in 1,2-dichlorocyclobuta-

Table 4.7

Comparison of Bond Distances(Å) and Angles (°) for Three Cyclopropabenzene Derivatives and Cyclopropa(b)napthalene



	a	b	c	d	e	max. esd Å	α	β	γ	δ	ε	max. esd °
(XII)	1.47	1.35	1.39	1.40	1.39	0.02	55.2	61.9	124	108.3	125	1
	1.45		1.42	1.38				62.9	128	109.7	125	
(XIII)	1.519	1.333	1.385	1.417	1.392	0.008	52.1	64.0	126.6	109.3	124.5	0.5
	1.520		1.389	1.421				64.0	126.3	109.6	123.6	
(XVa)*	1.536	1.352	1.375	1.384	1.396	0.02	52.0	62.9	125.6	113.4	121.4	1
	1.527		1.394	1.405				65.1	123.6	111.2	124.8	

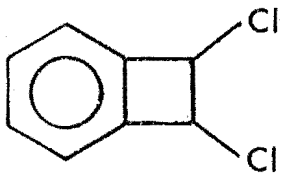
Table 4.7 contd.

	a	b	c	d	e	max. esd Å	α	β	γ	δ	ε	max. esd °
(XVb)	1.524	1.354	1.405	1.420	1.399	0.02	52.8	63.5	127.8	108.4	123.3	1
	1.520		1.374	1.408				63.7	124.2	111.8	124.5	
(XIV)‡	1.504	1.368	1.337	1.437	1.439	0.006	54.1	62.9	124.9	114.7	120.5	0.3

* two independent molecules in the asymmetric unit

‡ two halves of molecule related by a minor plane

benzene (XVI) (Hardgrove, Templeton and Templeton, 1968).



(XVI)

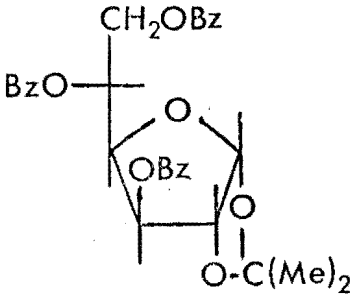
The carbon-chlorine distances of this molecule, 1.83(1)Å and 1.85(1)Å, are longer than those commonly observed in cycloalkabenzene and cycloalkanaphthalene derivatives (e.g. 1.774(8) and 1.785(8) in (XVI), 1.756(5) and 1.767(5) in a cyclopropa(b)napthalene derivative (Bordner and Howard, 1975)). However, longer distances have also been reported (e.g. 1.772(14)-1.865(17) and 1.756(10)-1.860(9) in two tetralin derivatives (Godfrey and Waters, 1973, 1975)). Further, the distances above for (XII) were corrected for thermal motion, a correction not reported to have been applied to the other distances quoted.

CHAPTER 5

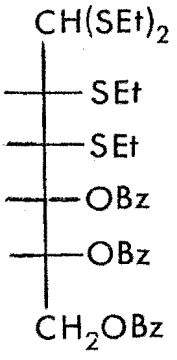
STRUCTURAL STUDY OF 4,5,6-TRI-O-BENZOYL-2,3-DI-S-ETHYL-2,3-DITHIO-D-ALLOSE DIETHYL DITHIOACETAL

5.1 INTRODUCTION

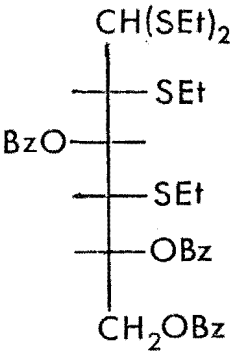
The reactions of peracylated sugars in the carbonyl form with ethane-thiol in the presence of acid catalysts result in diethyl dithioacetal formation as well as the replacement of acyloxy-groups. In an attempt to understand this process Bethell and Ferrier (1972a, 1972b, 1973) studied the products known to be formed on treatment of 3,5,6-tri-O-benzoyl-1,2-O-isopropylidene-α-D-glucofuranose (XVIII) under these conditions. Originally the product had been believed to be 3,5,6-tri-O-benzoyl-2,4-di-S-ethyl-2,4-dithio-D-glucose diethyl dithioacetal (XIX) (Brigl and Schinle, 1932). From their chemical and nmr analyses of this product they deduced that the compound was 4,5,6-tri-O-benzoyl-2,3-di-S-ethyl-2,3-dithio-D-allose diethyl dithioacetal (XVII). They proposed that the conversion



(XVIII)



(XVII)



(XIX)

from a sugar of the D-gluco series to a sugar of the D-allo series went via a manno-carbonium ion and involved three ester migrations with neighbouring group participation (Figure 5.1).* As each migration of a thio-group results in Walden inversion at the carbon atom to which the leaving group is attached, the net result is configurational inversion at C(3).

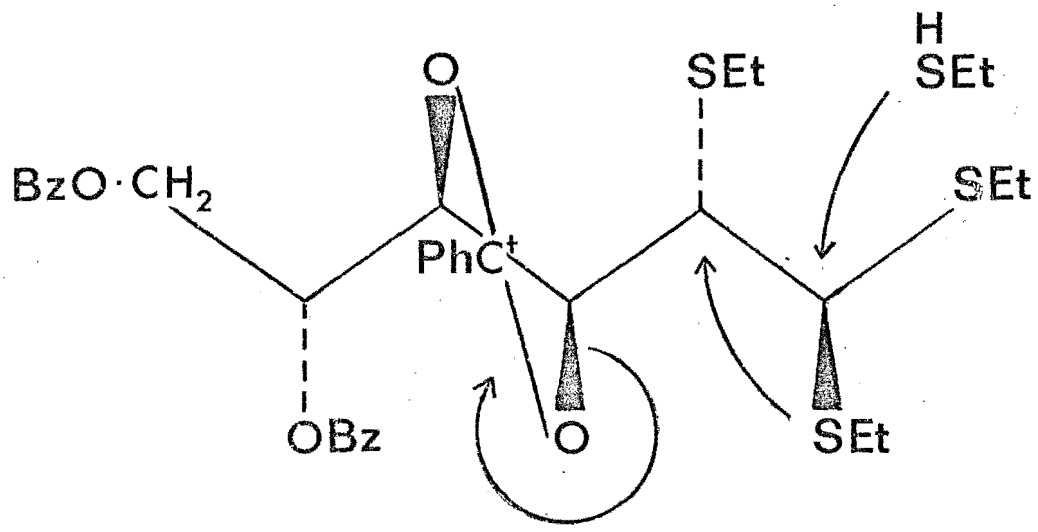


Figure 5.1

Proposed manno-intermediate with the pathway for the second and third ester migrations indicated

* Appendix 1 gives the configurations of aldoses of the D-series in their acyclic forms.

Evidence to support this hypothesis was obtained from an nmr coupling constant analysis of 1,4,6-tri-O-acetyl-2,3-di-S-ethyl-2,3-dithio-β-D-allopyranose (XXI) obtained from (XVII) by a four step process (Figure 5.2). There was however a slight possibility that the ring closure step to

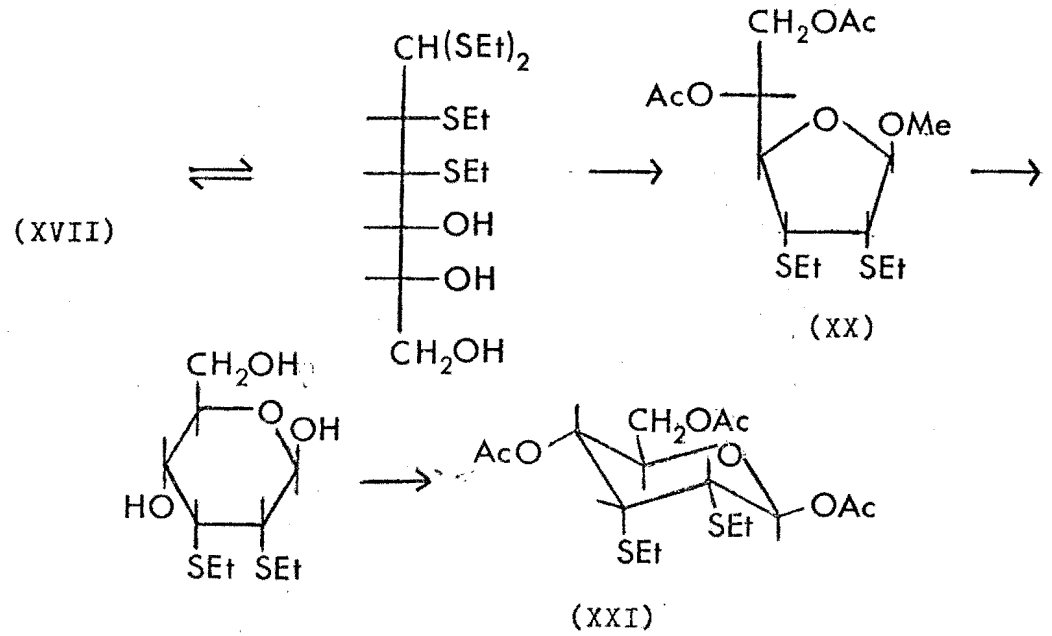


Figure 5.2

Proposed reaction pathway from the acyclic allose form to the allopyranose form

produce (XX) could have involved configurational conversion at C(2). Thus in order to verify their assignment of the molecular configuration as (XVII) this crystal structure analysis was undertaken. A preliminary study established the space group of this optically active compound as $P2_1$ and reflection data were collected in 1970 by Dr. Rachel Countryman. Two years later this author solved the structure using direct methods. The structure analysis confirmed that the compound has a D-allo configuration. Further, the conformation in the crystalline state is very

similar to the mean conformation in solution deduced from nmr spectra (Bethell and Ferrier, 1972a). A report of the structure has appeared in 'Acta Crystallographica' (McLennan, Robinson, Bethell and Ferrier, 1977).

5.2 EXPERIMENTAL

The compound was prepared by Dr. G.S. Bethell, Victoria University of Wellington, using the method reported previously (Bethell and Ferrier, 1972a). Colourless cyrstals suitable for X-ray diffraction studies were obtained by recrystallisation from ethanol.

The relevant crystal data are summarised in Table 5.1. The observed conditions limiting possible reflections (0k0, k=2n) are consistent with space groups $P2_1$ or $P2_1/m$. However the compound's optical activity restricted the space group to $P2_1$. This assignment was confirmed by the subsequent structure solution and refinements.

The diffraction data were collected using nickel filtered CuKα X-radiation. The experimental parameters are listed in Table 5.2 and the data collection and reduction procedures were as outlined in Chapter 2. The constancy of the intensities of the three standard reflections monitored throughout the data collection indicated there was no crystal deterioration. As the linear absorption coefficient is not high the data were not corrected for absorption.

Table 5.1

Crystal Data for $C_{35}H_{42}O_6S_4$

Formula	$C_{35}H_{42}O_6S_4$
Formula weight	686.97
System	Monoclinic
Space group	$P2_1$
a	9.185(1)Å
b	10.0160(8)Å
c	20.448(2)Å
β	99.29(1)°
V	1856.46Å
D_{calc}	1.23g cm^{-3}
Z	2
F(0,0,0)	728
μ(CuKα)	25.89 cm^{-1}

Table 5.2

Experimental Parameters for $C_{35}H_{42}O_6S_4$

Crystal dimensions	0.05 x 0.30 x 0.45 mm^3
Mosaicity	0.16-0.18°
θ scan range	0.60°
Scan time	60 sec.
Total background time	30 sec.
θ limit	50°
Total independent reflections	2402
Reflections used in final refinements for which $F_o^2 \geq 2\sigma(F_o^2)$	1519
Weighting paramenter p	0.116
Ratio of observations to parameters	4.4

5.3 SOLUTION AND REFINEMENT OF THE STRUCTURE

The structure was solved by direct methods using program MULTAN. The 2000 triplets of reflections, which satisfied the Σ_2 relationship with the highest probability, calculated from 367 normalised structure factors of magnitude ≥ 1.3, were used in the phase determination process. Two reflections were used in addition to the single one whose phase was determined by application of the Σ_1 relationship, and those needed to define the origin and the enantiomorph in the starting set for the tangent refinement procedure. This generated the four phase sets whose 'figures of merit' (Section 2.2.2) are given in Table 5.3.

Table 5.3

'Figures of Merit' from the Tangent Refinement Procedure for $C_{35}H_{42}O_6S_4$

set no.	absolute figure of merit	residual
1	1.00	0.40
2	1.28	0.37
3	1.10	0.38
4	1.23	0.35

A Fourier synthesis of the phased normalised structure factors corresponding to set 2 was calculated. Analysis of this E-map showed four peaks in likely positions for sulphur atoms and consistent with prominent vector peaks determined

by Patterson synthesis. In addition other peaks could be assigned as two possible oxygen atom positions and 12 other atom positions. Further, 16 out of the top 20 peaks were in chemically sensible positions. A structure factor calculation based on this model gave

$$R_1 = 0.459 \quad \text{and}$$
$$R_2 = 0.568.$$

From examination of subsequent least-squares refinement-difference Fourier synthesis cycles it was concluded that this was not the correct set of phases.

An E-map from the fourth set of phases yielded the correct solution. Assignment of the top four peaks as sulphur atom positions was consistent with the Patterson synthesis and two other high peaks appeared to indicate likely oxygen atom positions. It now became apparent why earlier attempts to solve the structure from the Patterson synthesis had been unsuccessful. Of the four peaks originally assumed to define Harker vectors for the four sulphur atoms, one peak actually resulted from superposition of two such vectors (relative height 86), another to a single sulphur atom (relative height 112), but the other two peaks (relative heights 96 and 86) did not relate to sulphur atom positions at all. The true Harker peak for the fourth sulphur atom is at approximately (0.5,0.5,0.5) and has a relative height of 157.

A structure factor calculation from the 1343 reflections for which $F_o^2 \geqslant 3\sigma(F_o^2)$, using the model derived from this second E-map (four sulphur atoms, two oxygen atoms and 12

other peaks incorporated as carbon atoms) gave conventional R-factors

$$R_1 = 0.407 \quad \text{and}$$
$$R_2 = 0.501.$$

In subsequent least-squares refinements the origin was fixed by holding the y co-ordinate of one of the sulphur atoms constant.

From an F_o Fourier synthesis calculated after two cycles of refinement it was possible to verify 17 of these positions, to distinguish four oxygen atoms originally refined as carbon atoms and to determine a further 19 carbon and oxygen atom positions. The remaining carbon atom positions were extracted by routine methods although difficulty was experienced in locating one phenyl ring and some ethyl carbon atoms. Refinements of this model, with isotropic thermal parameters assigned to all atoms and including the anomalous scattering of the sulphur atoms converged with

$$R_1 = 0.120 \quad \text{and}$$
$$R_2 = 0.137.$$

A structure factor calculation at this stage, for a model of opposite chirality, gave

$$R_1 = 0.125 \quad \text{and}$$
$$R_2 = 0.145.$$

thus demonstrating that each molecule does indeed have the '$\underline{\underline{D}}$' configuration.

In subsequent refinements anisotropic thermal

parameters were refined for the sulphur and terminal oxygen atoms and for the ethyl and phenyl carbon atoms. In order to refine all the parameters in these least-squares cycles it was necessary to use two large matrix blocks. In an attempt to gain greater precision of atomic parameters in the final refinements the 1519 reflections with $F_o^2 \geq 2\sigma$ were used. Because of the poor geometry and high temperature factors found for one phenyl ring (R ing 5 in Fig. 5.1) and the ethyl group carbons, C1a1 and C1a2, these were removed in successive least-square refinement and new positions established from difference Fourier syntheses. These new positions, after several cycles of refinement, were not significantly different from the original positions. This model converged with

$$R_1 = 0.092 \quad \text{and}$$
$$R_2 = 0.097.$$

An examination of current structure factor magnitudes indicated that $\Sigma w(|F_o|-|F_c|)^2$ increased systematically with increasing magnitude of the structure factors. The data was reprocessed using a 'p' value of 0.116 (the original 'p' factor was 0.050).

Because eight, low-angle reflections showed evidence of extinction, an extinction parameter was refined (Zachariasen, 1963,1967), and in every case resulted in significant improvement in these descrepancies between calculated and observed structure factors. The final value of the extinction parameter was $0.7(2) \times 10^{-6}$. This model converged with

$$R_1 = 0.092 \quad \text{and}$$
$$R_2 = 0.108$$

and for all 2042 reflections collected

$$R_1 = 0.123 \quad \text{and}$$
$$R_2 = 0.116.$$

In the final cycle of refinement the largest shift was 0.62σ (in U_{13} of C1a2) and the average shift was 0.07σ. The standard error in an observation of unit weight is 1.47.

The highest peaks in a final difference Fourier synthesis correspond to positions of hydrogen atoms bonded to central chain carbon atoms, with a maximum calculated electron density ($0.38 e\text{Å}^{-3}$) of about one third of the height of the last carbon atom located by such methods. In the interests of economy and because of the limited data hydrogen atom positions were not included in structure factor calculations. Co-ordinates were derived for those seven hydrogen atoms which are attached to the carbon atoms of the central chain using program TETRIG. The final positional and thermal parameters of all non-hydrogen atoms are given in Table 5.4 and the calculated hydrogen atom co-ordinates are listed in Table 5.5. A full listing of final structure factors is given in Appendix 4.

5.4 DESCRIPTION OF THE STRUCTURE

The molecule has a D-allo-configuration and a bent, ziz-zig carbon chain conformation as illustrated in the perspective views, Figures 5.3a and 5.3b which also give the

Table 5.4

Positional Parameters ($x10^4$), Isotropic and Anisotropic Parameters ($x10^2$)

for the Non-hydrogen Atoms of $C_{35}H_{42}O_6S_4$

	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S(1a)	991(5)	299(7)	6781(2)	8.9(3)	12.1(4)	10.9(4)	-3.0(3)	1.9(3)	-0.4(3)
S(1b)	2456(6)	2714	7448(3)	12.5(4)	9.6(4)	12.3(4)	1.6(3)	2.6(3)	-1.7(3)
S(2)	3373(5)	-123(6)	8170(2)	9.6(3)	9.7(4)	6.6(2)	-2.7(3)	3.8(3)	-0.1(2)
S(3)	5912(5)	1540(6)	6690(2)	10.4(3)	8.5(3)	6.8(2)	-2.8(3)	3.0(2)	0.3(2)
O(4)	7846(9)	1060(10)	8212(4)	6.1(2)					
O(41)	6845(10)	993(12)	9141(4)	8.9(7)	11.5(9)	6.4(6)	-4.3(7)	3.0(5)	-2.0(6)
O(5)	6487(10)	-1558(10)	7079(5)	6.7(3)					
O(51)	8021(13)	-1780(15)	6359(6)	13(1)	15(1)	12.2(9)	-6(1)	6.9(8)	-5.6(9)
O(6)	7971(11)	-2345(13)	8399(5)	8.6(3)					
O(61)	7616(16)	-4136(13)	7752(6)	19(1)	8.4(9)	8.4(8)	-2.3(9)	5.6(8)	-2.8(7)
C(1)	2735(17)	1212(19)	6955(8)	8.5(5)					
C(1a1)	1299(50)	-429(59)	5864(29)	18(4)	31(6)	33(7)	-13(4)	5(4)	-12(5)

Table 5.4 contd.

	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1a2)	775(76)	580(98)	5585(39)	34(6)	50(10)	47(8)	4(7)	-18(5)	15(8)
C(1b1)	1497(35)	3633(25)	6819(14)	25(3)	7(2)	18(2)	4(2)	2(2)	-1(2)
C(1b2)	1045(36)	4978(36)	7127(15)	22(3)	17(3)	20(3)	4(3)	2(2)	-0(2)
C(2)	3928(15)	313(16)	7372(6)	6.6(4)					
C(21)	3214(27)	-1966(21)	8068(10)	20(2)	7(1)	11(1)	-1(1)	5(1)	1(1)
C(22)	2718(20)	-2515(24)	8698(8)	12(1)	14(2)	8(1)	1(1)	4(1)	3(1)
C(3)	5433(14)	1017(15)	7492(6)	6.0(4)					
C(31)	7044(27)	2983(20)	6912(11)	21(2)	7(1)	14(2)	-7(1)	8(2)	-2(1)
C(32)	7344(27)	3614(22)	6250(12)	18(2)	9(1)	16(2)	-3(1)	5(2)	5(1)
C(4)	6669(15)	138(16)	7897(7)	6.8(4)					
C(41)	7760(14)	1415(14)	8852(6)	5.4(3)					
C(42)	8903(15)	2390(13)	9095(6)	6.8(9)	4.7(9)	5.9(8)	0.3(7)	-0.4(7)	0.4(7)
C(43)	8826(20)	3057(19)	9714(7)	12(1)	9(1)	5.1(9)	1(1)	-0.1(8)	-0.1(9)
C(44)	9949(24)	3968(19)	9931(10)	10(1)	7(1)	8(1)	-0(1)	-3(1)	-2(1)
C(45)	11018(20)	4329(18)	9597(9)	10(1)	8(1)	9(1)	-3(1)	1(1)	2(1)

Table 5.4 contd.

	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(46)	11120(21)	3731(23)	8989(8)	11(1)	14(2)	7(1)	-7(1)	-1(1)	-2(1)
C(47)	10001(16)	2749(17)	8717(7)	8(1)	7(1)	9(1)	-1(1)	3.3(9)	-1(1)
C(5)	7597(14)	-730(16)	7486(6)	6.1(4)					
C(51)	6893(17)	-1962(17)	6493(7)	8.0(5)					
C(52)	5736(21)	-2788(17)	6092(7)	12(1)	6(1)	8(1)	-1(1)	3(1)	0.6(9)
C(53)	5990(29)	-3154(22)	5473(9)	22(2)	11(2)	5(1)	-2(2)	3(1)	-0(1)
C(54)	5021(47)	-3897(33)	5059(12)	24(3)	15(2)	8(1)	-1(3)	-4(2)	-2(2)
C(55)	3691(38)	-4217(29)	5234(15)	19(3)	12(2)	16(3)	-3(2)	-0(2)	-5(2)
C(56)	3313(35)	-3814(39)	5838(16)	21(3)	25(4)	20(3)	-9(3)	7(2)	13(3)
C(57)	4425(29)	-3000(31)	6275(12)	16(2)	19(3)	14(2)	-9(2)	5(2)	-9(2)
C(6)	8668(17)	-1653(18)	7914(8)	8.2(5)					
C(61)	7400(16)	-3596(18)	8259(7)	7.4(4)					
C(62)	6695(16)	-4137(18)	8793(8)	7(1)	7(1)	9(1)	1(1)	1.2(8)	1.4(9)
C(63)	5866(20)	-5314(19)	8621(9)	10(1)	7(1)	11(1)	-1(1)	3(1)	2(1)
C(64)	5160(21)	-5816(20)	9085(12)	10(1)	8(1)	14(2)	4(1)	0(1)	-0(1)

Table 5.4 contd.

	x	y	z	U or U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(65)	5240(25)	-5252(27)	9721(11)	12(2)	11(2)	10(2)	3(1)	2(1)	2(1)
C(66)	6060(23)	-4126(28)	9904(9)	12(2)	13(2)	9(1)	2(2)	1(1)	-4(2)
C(67)	6767(19)	-3555(17)	9413(7)	13(1)	8(1)	6.1(9)	3(1)	3(1)	-2(1)

Table 5.5

Positional Parameters (x 10^3) for the Hydrogen Atoms of $C_{35}H_{42}O_6S_4$

	x	y	z
H(1)	305	146	655
H(2)	402	-49	713
H(3)	534	180	775
H(4)	625	-39	820
H(5)	812	-17	722
H(6a)	903	-229	764
H(6b)	946	-114	814

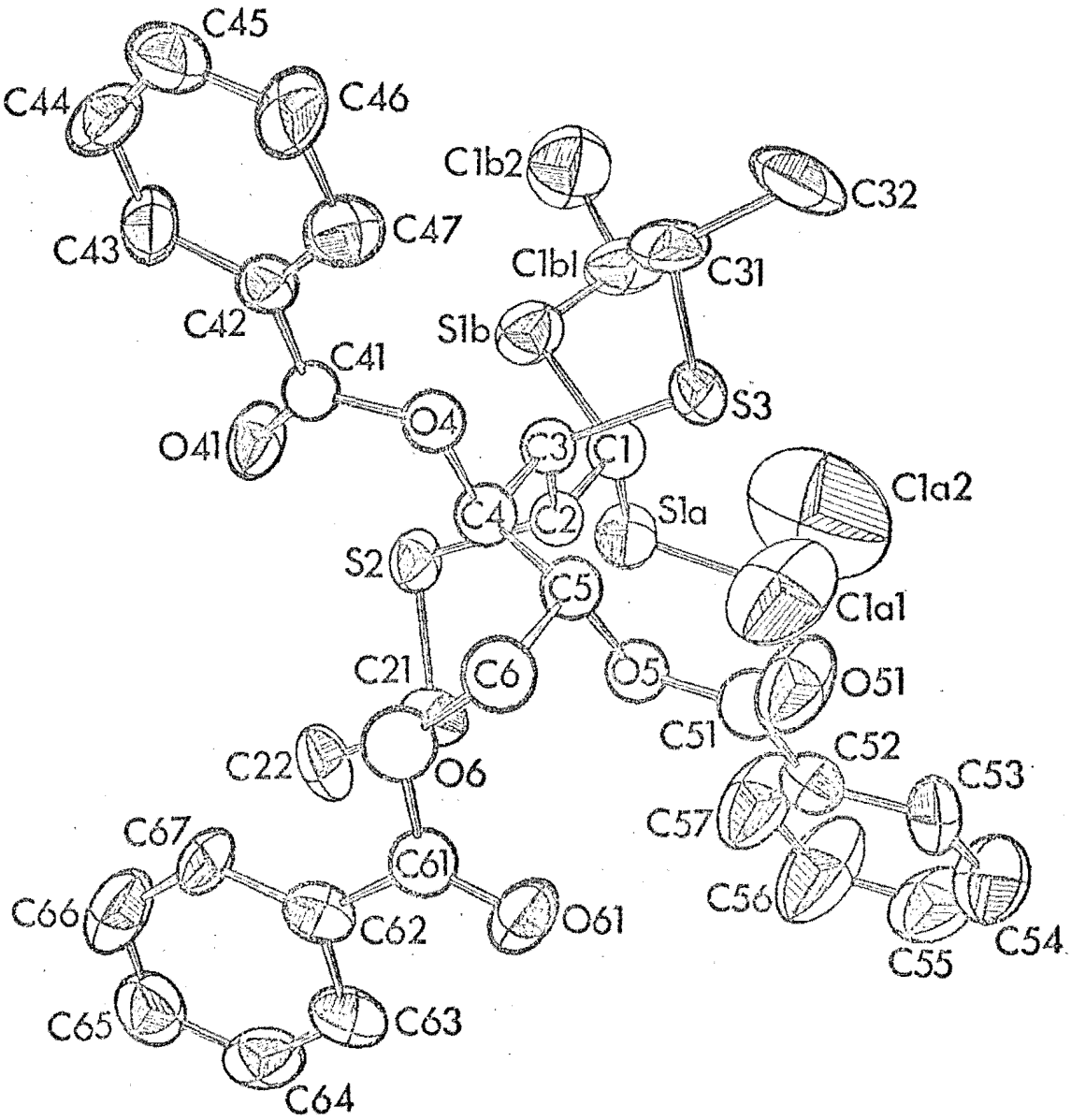


Figure 5.3a

A perspective view of one molecule of $C_{35}H_{42}O_6S_4$

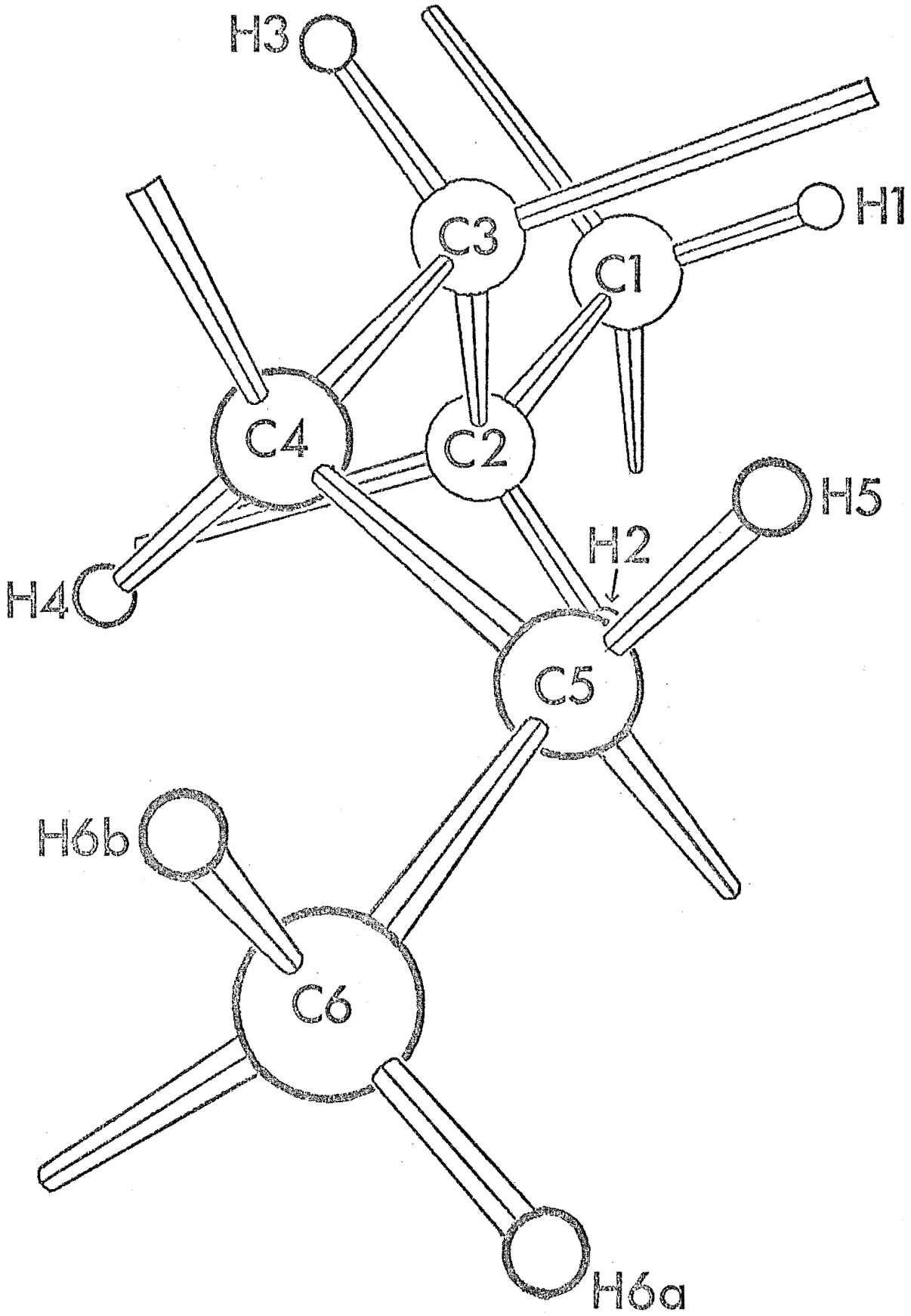


Figure 5.3b

An enlargement of Figure 5.3a showing the hydrogen atoms attached to the central carbon chain

atom numbering scheme. Figure 5.4 shows the observed conformational angles about the allo-chain and Table 5.6 lists torsional angles for the complete molecule. Bond distances and angles are given in Tables 5.7 and 5.8. None of the distances has been corrected for thermal motion.

From Figure 5.3a it is apparent that the terminal ethyl group atoms C(1a1) and C(1a2) have very high thermal motion. Such effects in terminal ethyl and methyl groups attached to sulphur atoms are not uncommon (e.g. Ducruix and Pascard-Billy, 1974; Stenkamp and Jansen, 1975)). The S(1a)-C(1a1) and C(1a1)-C(1a2) bond distances and the S(1a)-C(1a1)-C(1a2) bond angle are, consequently, not very reliable values.

Acyclic allose derivatives with fully-staggered planar carbon chains have C(n)-C(n+1)....C(n+2)-C(n+3) (n = 1,2 or 3) torsional angles of 180°. In this derivative the C(2)-C(3)....C(4)-C(5) angle is 93° giving a bent carbon atom chain. Atoms S(1a),C(1),C(2),C(3) and C(4) all lie within 0.042Å of a plane and atoms C(3),C(4),C(5) and C(6) lie within 0.037Å of a second plane (Table 5.9a). The angle between these two planes is 88°. The conformation can therefore be described as that obtained by a rotation around C(3)-C(4), of about 88°, away from the planar zig-zag. Consequently, the spatial arrangement of bonds about C(3)-C(4), is not fully staggered (Figure 5.4).

An analysis of mean planes through the O-benzoyl substituents is given in Table 5.9b. The O-benzoyl group attached to C(5) is only approximately planar but in the other two groups there are significant twists between the plane

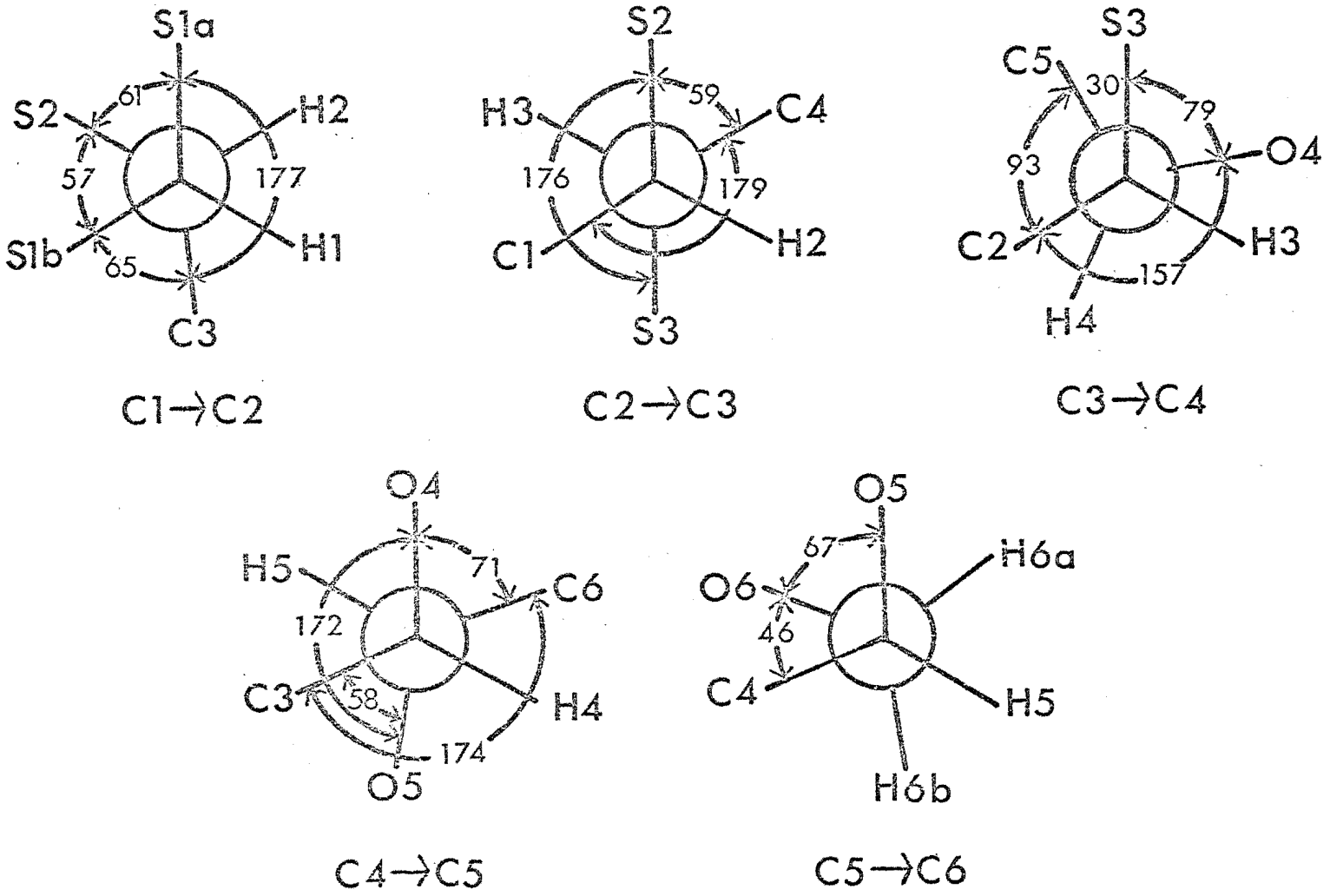


Figure 5.4

Conformational angles (°) about the carbon-carbon bonds of the central chain in $C_{35}H_{42}O_6S_4$

Table 5.6

Selected Torsional Angles (°) in $C_{35}H_{42}O_6S_4$

S(1a)-C(1) ....C(2) -S(2)	-61.4	C(41)-C(42)....C(43)-C(44)	179.2
S(1a)-C(1) ....C(2) -C(3)	176.5	C(47)-C(42)....C(43)-C(44)	-5.1
S(1b)-C(1) ....C(2) -S(2)	57.0	C(42)-C(43)....C(44)-C(45)	4.5
S(1b)-C(1) ....C(2) -C(3)	-65.1	C(43)-C(44)....C(45)-C(46)	-3.3
S(2) -C(2) ....C(3) -S(3)	-176.4	C(44)-C(45)....C(46)-C(47)	2.4
S(2) -C(2) ....C(3) -C(4)	58.7	C(45)-C(46)....C(47)-C(42)	-3.2
C(1) -C(2) ....C(3) -S(3)	-53.9	C(46)-C(47)....C(42)-C(41)	-179.9
C(1) -C(2) ....C(3) -C(4)	-178.8	C(46)-C(47)....C(42)-C(43)	4.6
S(3) -C(3) ....C(4) -O(4)	79.5	C(51)-C(52)....C(53)-C(54)	-179.6
S(3) -C(3) ....C(4) -C(5)	-30.2	C(57)-C(52)....C(53)-C(54)	-9.3
C(2) -C(3) ....C(4) -O(4)	-157.2	C(52)-C(53)....C(54)-C(55)	5.2
C(2) -C(3) ....C(4) -C(5)	93.1	C(53)-C(54)....C(55)-C(56)	-1.1
O(4) -C(4) ....C(5) -O(5)	-172.2	C(54)-C(55)....C(56)-C(57)	1.0
O(4) -C(4) ....C(5) -C(6)	71.3	C(55)-C(56)....C(57)-C(52)	-4.8
C(3) -C(4) ....C(5) -O(5)	-57.8	C(56)-C(57)....C(52)-C(51)	178.6

Table 5.6 contd.

C(3) -C(4) ....C(5) -C(6)	-174.3	C(56)-C(57)....C(52)-C(53)	8.8
O(5) -C(5) ....C(6) -O(6)	-67.3	C(61)-C(62)....C(63)-C(64)	-177.7
C(4) -C(5) ....C(6) -O(6)	46.4	C(67)-C(62)....C(63)-C(64)	0.5
O(4) -C(41)....C(42)-C(43)	169.3	C(62)-C(63)....C(64)-C(65)	-1.6
O(4) -C(41)....C(42)-C(47)	-6.4	C(63)-C(64)....C(65)-C(66)	0.4
O(41)-C(41)....C(42)-C(43)	-8.8	C(64)-C(65)....C(66)-C(67)	2.0
O(41)-C(41)....C(42)-C(47)	175.6	C(65)-C(66)....C(67)-C(62)	-3.0
O(5) -C(51)....C(52)-C(53)	175.0	C(66)-C(67)....C(62)-C(61)	179.8
O(5) -C(51)....C(52)-C(57)	4.8	C(66)-C(67)....C(62)-C(63)	1.9
O(51)-C(51)....C(52)-C(53)	-11.1	C(4) -O(4) ....C(41)-O(41)	2.1
O(51)-C(51)....C(52)-C(57)	178.7	C(4) -O(4) ....C(41)-C(42)	-176.1
O(6) -C(61)....C(62)-C(63)	169.3	C(5) -O(5) ....C(51)-O(51)	6.6
O(6) -C(61)....C(62)-C(67)	-8.8	C(5) -O(5) ....C(51)-C(52)	-179.5
O(61)-C(61)....C(62)-C(63)	-16.2	C(6) -O(6) ....C(61)-O(61)	6.6
O(61)-C(61)....C(62)-C(67)	165.8	C(6) -O(6) ....C(61)-C(62)	-178.2
C(1)-S(1a) ....C(1a1)-C(1a2)	-86.6	C(21)-S(2) ....C(2) -C(1)	116.9

Table 5.6 contd.

C(1a1)-S(1a)....C(1) -S(1b)	147.5	C(21)-S(2) ....C(2) -C(3)	-120.4
C(1a1)-S(1a)....C(1) -C(2)	-94.2	C(2) -S(2) ....C(21)-C(22)	-178.9
C(1) -S(1b) ....C(1b1)-C(1b2)	177.2	C(31)-S(3) ....C(3) -C(2)	151.2
C(1b1)-S(1b)....C(1) -S(1a)	-74.8	C(31)-S(3) ....C(3) -C(4)	-83.5
C(1b1)-S(1b)....C(1) -C(2)	166.3	C(3) -S(3) ....C(31)-C(32)	-172.9

Table 5.7

Interatomic Distances (Å) in $C_{35}H_{42}O_6S_4$

S(1a)-C(1)	1.83(2)	C(1)-C(2)	1.56(2)
S(1a)-C(1a1)	2.07(5)	C(2)-C(3)	1.54(2)
S(1b)-C(1)	1.85(2)	C(3)-C(4)	1.56(2)
S(1b)-C(1b1)	1.71(3)	C(4)-C(5)	1.56(2)
S(2)-C(2)	1.84(1)	C(5)-C(6)	1.52(2)
S(2)-C(21)	1.86(2)		
S(3)-C(3)	1.84(1)	C(1a1)-C(1a2)	1.22(9)
S(3)-C(31)	1.80(2)	C(1b1)-C(1b2)	1.57(4)
		C(21)-C(22)	1.54(2)
C(41)-O(41)	1.18(1)	C(31)-C(32)	1.56(3)
C(51)-O(51)	1.13(2)		
C(61)-O(61)	1.21(2)	C(41)-C(42)	1.46(1)
		C(51)-C(52)	1.49(2)
C(41)-O(4)	1.37(1)	C(61)-C(62)	1.46(2)
C(51)-O(5)	1.37(2)		
C(61)-O(6)	1.37(2)	C(4)-O(4)	1.49(2)
		C(5)-O(5)	1.46(2)
		C(6)-O(6)	1.44(2)
C-C(Ph4)	1.33(3)-1.47(2)		
C-C(Ph5)	1.34(2)-1.49(3)		
C-C(Ph6)	1.33(2)-1.42(2)		

Table 5.8

Bond Angles(°) in $C_{35}H_{42}O_6S_4$

C(1)-S(1a)-C(1a1)	96(1)	O(41)-C(41)-C(42)	127(1)
C(1)-S(1b)-C(1b1)	97(1)	O(51)-C(51)-C(52)	124(1)
C(2)-S(2)-C(21)	99.5(8)	O(61)-C(61)-C(62)	129(1)
C(3)-S(3)-C(31)	102.4(8)		
S(1a)-C(1a1)-C(1a2)	92(6)	O(4)-C(41)-O(41)	123(1)
S(1b)-C(1b1)-C(1b2)	107(2)	O(5)-C(51)-O(51)	124(1)
S(2)-C(21)-C(22)	107(1)	O(6)-C(61)-O(61)	118(1)
S(3)-C(31)-C(32)	106(1)		
		C(4)-O(4)-C(41)	115.2(9)
S(1a)-C(1)-S(1b)	108.6(8)	C(5)-O(5)-C(51)	114(1)
S(1a)-C(1)-C(2)	109(2)	C(6)-O(6)-C(61)	120(1)
S(1b)-C(1)-C(2)	109(1)		
S(2)-C(2)-C(1)	110.6(9)	C(41)-C(42)-C(43)	118(1)
S(2)-C(2)-C(3)	109.8(8)	C(41)-C(42)-C(47)	121(1)
S(3)-C(3)-C(2)	109.1(8)	C(51)-C(52)-C(53)	116(2)
S(3)-C(3)-C(4)	112.0(9)	C(51)-C(52)-C(57)	122(2)
		C(61)-C(62)-C(63)	114(2)
C(1)-C(2)-C(3)	111(1)	C(61)-C(62)-C(67)	124(2)
C(2)-C(3)-C(4)	113(1)		
C(3)-C(4)-C(5)	116(1)	O(4)-C(41)-C(42)	110(1)
C(4)-C(5)-C(6)	113(1)	O(5)-C(51)-C(52)	112(1)
		O(6)-C(61)-C(62)	113(1)
O(4)-C(4)-C(3)	107(1)		
O(4)-C(4)-C(5)	99.1(9)	C-C-C (Ph4)	116(2) - 126(2)
O(5)-C(5)-C(4)	103(1)	C-C-C (Ph5)	117(3) - 122(3)
O(5)-C(5)-C(6)	108(1)	C-C-C (Ph6)	116(2) - 123(2)
O(6)-C(6)-C(5)	112(1)		

Table 5.9(a)

Least-squares Planes of Allose Chain of $C_{35}H_{42}O_6S_4$

(i) Atoms defining planes and distances of atoms from planes (Å)

plane 1		plane 2		plane 3	
C(1)	-0.007	S(1a)	0.024	C(3)	0.035
C(2)	-0.008	C(1)	-0.042	C(4)	-0.037
C(3)	0.007	C(2)	0.015	C(5)	-0.032
C(4)	0.007	C(3)	-0.010	C(6)	0.035
		C(4)	0.014		

(ii) Interplanar angles (°)

1-2	2.67°	2-3	87.77°	1-3	85.03°

(iii) Distances of other atoms from planes (Å)

	plane 1	plane 2	plane 3
S(1a)	0.11	-	3.24
S(1b)	-1.58	-1.55	0.64
H(1)*	0.75	0.76	1.07
C(1)	-	-	1.50
S(2)	-1.47	-1.56	2.25
H(2)*	0.78	0.72	1.97
C(2)	-	-	1.47
S(3)	1.41	1.48	-0.75
H(3)*	-0.82	-0.77	-0.45
O(4)	-0.54	-0.48	-1.41
H(4)*	-0.48	-0.51	0.65
O(5)	2.11	2.06	1.21

Table 5.9(a) contd.

H(5)*	1.84	1.88	-0.81
C(5)	1.41	1.41	-
O(6)	0.50	0.42	1.04
H(6a)*	2.21	2.18	0.24
H(6b)*	0.98	1.00	-0.81
C(6)	1.34	1.32	-

* calculated positions only

Table 5.9(b)

Least-squares Planes of O-Benzoyl Substituents of $C_{35}H_{42}O_6S_4$

(i) Atoms defining planes and distances of the atoms from planes (Å)

plane 1		plane 4		plane 7	
O(4)		O(5)		O(6)	
C(41)		C(51)		C(61)	
O(41)		O(51)		O(61)	
plane 2		**plane 5**		**plane 8**	
O(4)	0.003	O(5)	-0.009	O(6)	-0.008
C(41)	-0.010	C(51)	0.031	C(61)	0.026
O(41)	0.004	O(51)	-0.013	O(61)	-0.010
C(42)	0.003	C(52)	-0.009	C(62)	-0.008
plane 3		**plane 6**		**plane 9**	
C(42)	-0.022	C(52)	-0.044	C(62)	-0.002
C(43)	0.021	C(53)	0.030	C(63)	-0.010
C(44)	-0.013	C(54)	-0.004	C(64)	0.009
C(45)	0.006	C(55)	-0.009	C(65)	0.004
C(46)	-0.006	C(56)	-0.004	C(66)	-0.015
C(47)	0.015	C(57)	0.030	C(67)	0.015

(ii) Interplanar angles (°)

1-2	1.24	1-3	8.19	2-3	7.83
4-5	4.14	4-6	4.35	5-6	2.89
7-8	3.08	7-9	12.73	8-9	12.61
3-6	13.04	3-9	18.93	6-9	30.78

Table 5.9(b) contd.

(iii) Distances of other atoms from selected planes (Å)

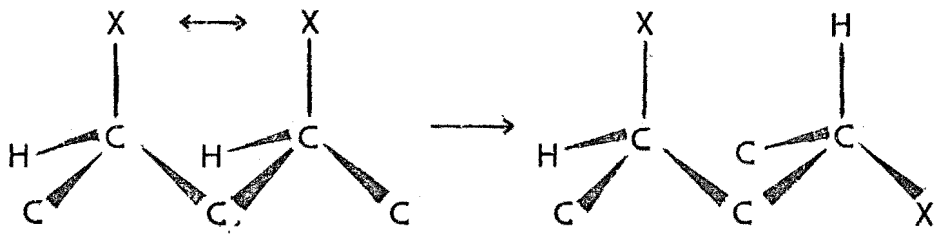
plane 2		plane 5		plane 8	
C(4)	0.085	C(5)	0.039	C(6)	0.058
C(43)	0.229	C(53)	0.133	C(63)	0.266
C(44)	0.217	C(54)	0.122	C(64)	0.293
C(45)	0.100	C(53)	0.072	C(65)	0.035
C(46)	-0.093	C(56)	0.008	C(66)	-0.258
C(47)	-0.109	C(57)	0.020	C(67)	-0.243

of the phenyl atoms and the approximate plane of the other atoms in the group. Similar twists have been observed in the O-benzoyl groups in tri-O-benzoyl-β-D-xylopyranosyl bromide (Luger, Durette and Paulsen, 1974).

The molecular packing is illustrated in a stereoscopic view of the contents of two unit cells viewed down the shortest axis (Figure 5.5). The molecules are well separated with the only inter-molecular contacts not involving hydrogen and less than 3.5Å being O(61)-C(31) (3.36Å) and S(1a)-O(51) (3.43Å).

5.5 DISCUSSION

The favoured conformation for acyclic aldose derivatives is the extended planar zig-zag arrangement except where this gives rise to parallel interactions between substituents on alternate carbon atoms. In such cases, rotations of 120° about one or more carbon-carbon bonds from the planar zig-zag (A) to give a bent-chain non-planar carbon chain (B), are expected. This hypothesis was developed (Jeffrey and



(A) (B)

Kim, 1970) from observations of the crystal structures of a number of alditols (DL-arabinitol (Hunter and Rosenstein,

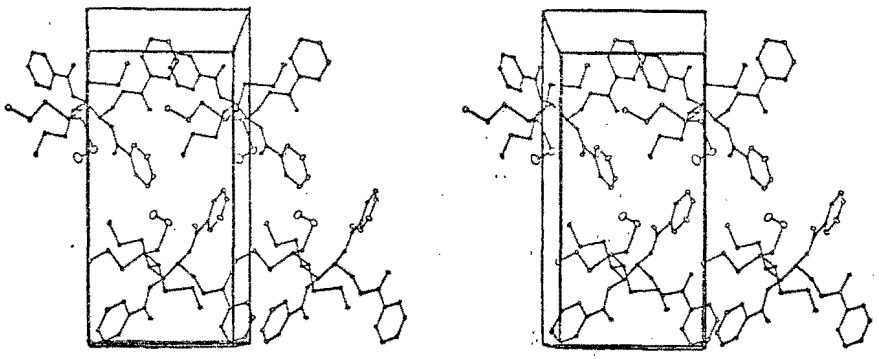


Figure 5.5

Packing of molecules of $C_{35}H_{42}O_6S_4$

View is down the a axis with the b axis horizontal

1968), ribitol (Kim, Jeffrey and Rosenstein, 1969), xylitol (Kim and Jeffrey, 1969), D-mannitol ((Berman, Jeffrey and Rosenstein, 1968); (Kim, Jeffrey and Rosenstein, 1968)), galacitol (Berman and Rosenstein, 1968), D-glucitol (Park and Jeffrey, 1971), D-glucitol-pyridine (Snyder, Rosenstein, Kim and Jeffrey, 1970) and D-iditol (Azarnia, Jeffrey and Shen, 1972)). It is also consistent with nmr solution studies of acyclic sugar derivatives ((Horton and Miller, 1965), (El Khadem, Horton and Page, 1968) and (Horton and Wander, 1969)).

In allose derivatives, then, a planar zig-zag conformation (e.g. Fig. 5.6a) would give interactions between substituents at C(2), C(4) and C(3), C(5). In allitol (Azarnia, Jeffrey and Shen, 1972) the conformation can be described as having been obtained by two rotations of 120° about C(2)-C(3) and C(4)-C(5) away from a planar zig-zag (Fig. 5.6c). In this tetra-thio derivative there is a single rotation and it is about C(3)-C(4). This conformation appears to be a direct consequence of the molecular configuration rather than any crystal packing effects.

Whereas in allitol there is a fully staggered conformer (Figure 5.6c) that does not involve eclipsing interactions, in this derivative, because there are two bulky thio-groups attached to C(1) a different situation arises. First of all consider the staggered arrangements about the C(2)-C(3) bond. In a planar zig-zag (i.e. C(1)-C(2)....C(3)-C(4) torsional angle is 180°) a C(2)-S(2)/C(4)-O(4) interaction occurs (Figure 5.6a). In an allitol-like conformer (C(2)-C(3).... C(4)-C(5) torsional angle is -60°) either a C(1)-S(1b)/

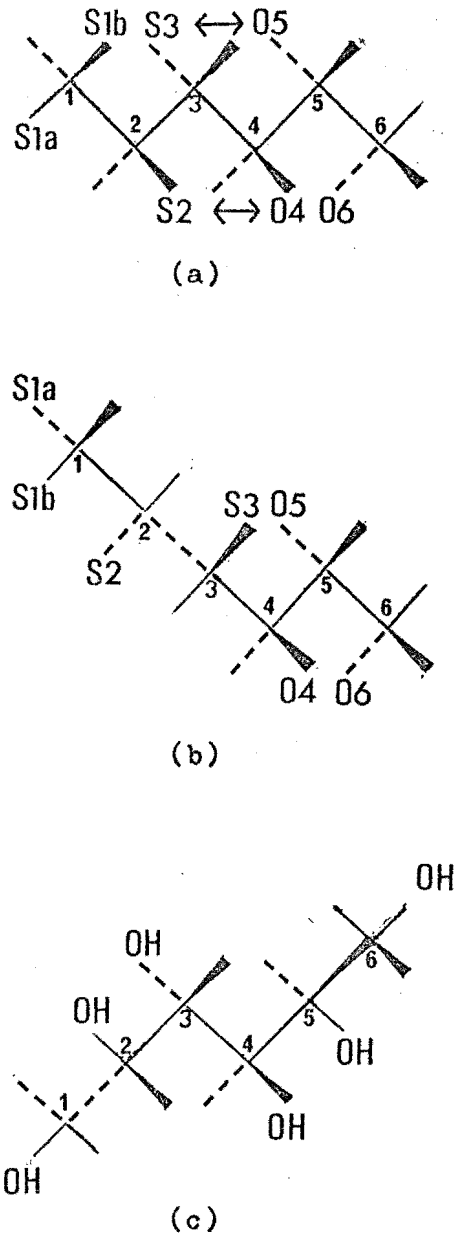


Figure 5.6

Conformations of acyclic allose derivatives

(a) Tetra-thio derivative in extended planar zig-zag form

(b) Tetra-thio derivative in conformation obtained by a rotation of 120° about C(3)-C(4) from (a).

(c) The conformation of allitol predicted and observed by Azarnia, Jeffrey and Shen (1972).

C(3)-S(3) or a C(1)-(S1a)/C(3)-C(4) interaction must occur. A further rotation of 120° about C(2)-C(3) is also unfavourable because of a resulting C(2)-C(1)/C(4)-O(4) parallel interaction. This arrangement would also bring O(4) close to a sulphur atom at C(1). Similarly, each of the three distinct staggered arrangements of bonds about C(3)-C(4) leads to steric interactions. In extended planar zig-zag forms the C(3)-S(3) and C(5)-O(5) bonds overlap. A rotation of 120° away from the planar zig-zag so that the C(2)-C(3)....C(4)-C(5) angle is -60° gives a C(2)-S(2)/C(4)-C(5) interaction, and a rotation in the other direction parallel C(3)-C(2) and C(5)-O(5) bonds (Figure 5.6b).

It is not surprising, therefore, that the observed conformer is similar to Figure 5.5b but where the C(2)-C(3)....C(4)-C(5) torsional angle is 93° rather than the 60° expected for a fully-staggered, bent chain. This avoids the C(3)-C(2) bond eclipsing the C(5)-O(5) bond. (The C(2)-O(5) distance is 3.14Å compared with approximately 2.6Å for eclipsed atoms.) Nor is it surprising that S(1a) is in the plane of the carbon atoms C(1), C(2), C(3) and C(4), as this is the only staggered rotamer about C(1) that does not result in steric interactions between S(3) and S(1a) or S(1b). However the spatial arrangement of the sulphur atoms does result in short non-bonded intramolecular distances S(1a)-S(2) and S(1b)-S(2) (Table 5.10) compared with the Van der Waal's radius of sulphur (1.85Å (Pauling, 1960)). Other short intramolecular contacts of the sulphur atoms (within 3.5Å) and non-benzoyl carbon and oxygen atoms (within 3.0Å) are also given in Table 5.10. Distances

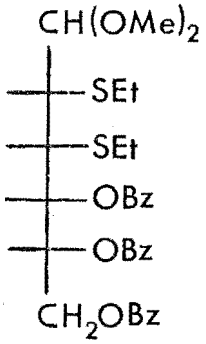
Table 5.10

Intramolecular Non-bonded Distances (Å) in $C_{35}H_{42}O_6S_4$

S(1a)-S(2)	3.32	S(3)-O(5)	3.23
S(1a)-C(1b1)	3.37	S(3)-O(4)	3.36
S(1b)-C(3)	3.21	O(4)-C(6)	2.91
S(1b)-S(2)	3.25	O(5)-C(3)	2.93
S(2)-C(4)	3.18	O(5)-O(6)	2.93
S(3)-C(5)	3.07	O(6)-C(4)	2.88
S(3)-C(1)	3.07		

involving hydrogen atoms or between atoms bonded to a common atom are not given. Similar conformational crowding has been reported in the crystal structure of 2-S-ethyl-2-thio-D-mannose diethyl dithioacetal (Ducruix and Pascard-Billy, 1974).

The favoured conformation of this tetra-thio allose derivative in solution, as deduced from nmr analysis, is very similar (Bethell and Ferrier, 1972a). Their nmr studies also included the dimethyl acetal allose derivative (XXII). They suggested, interestingly, that the mean conformer of this compound does have two bends in the zig-zag chain, similar to the structure observed for allitol.



(XXII)

Useful discussion of the bond distances and angles is restricted by their low precision which is, of course, a consequence of the limited reflection data collected. The mean carbon-carbon distance of the chain atoms is 1.55(1)Å and the mean carbon-carbon-carbon angle is 113(1)°. This bond distance is significantly longer than that typically observed in the alditols (about 1.52Å, e.g.(Jeffrey and Kim, 1970 ; Azarnia, Jeffrey and Shen, 1972)), but the bond angle agrees well. The C(3)-C(4)-C(5) angle of 116(1)° is larger than usual and the O(4)-C(4)-C(5) and O(5)-C(5)-C(4) angles of 99.1(9)° and 103(1)°, respectively, are smaller than are typically observed in the alditols. The usual substituent-carbon-carbon bond angles are about 109°. The differences in bond distances and angles from the alditols are not surprising in view of (a) the greater substitution of the central carbon chain in this compound and (b) the consequent impossibility of it crystallising in a fully staggered conformation without eclipsing interactions resulting.

The carbon-sulphur distances with the exception of S(1b)-C(1b1) and S(1a)-C(1a1) are similar to values observed in other thio-sugar derivatives which range from 1.76-1.88Å (Ducruix and Pascard-Billy, 1972, 1974; Girling and Jeffrey, 1973, 1974; Beale, Stephenson and Stevens, 1972). The mean carbon-sulphur distance is 1.84(3)Å. The C(51)-O(51) bond is short but probably not significantly different from the C(41)-O(41) and C(61)-O(61) distances. Other distances and angles in the O-benzoyl substituents agree well with those reported for 4,5,6-tri-O-benzoyl-β-D-xylopyranosyl bromide.

(Luger, Durette and Paulsen, 1974) and 2,3,4-tri-O-benzoyl-β-D-xylopyranosyl chloride (Luger, Kothe and Paulsen, 1976).

CHAPTER 6

STRUCTURAL STUDY OF THYRSIFERYL ACETATE

6.1 INTRODUCTION

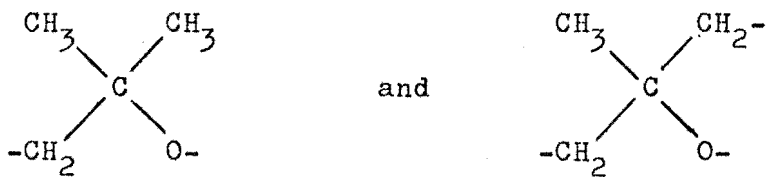
Until comparatively recently little has been known about marine natural products. As a result of world wide interest in the oceans as a source of pharmaceutical chemicals this situation is gradually being corrected. Pharmacological properties have been observed in a wide range of such natural products. Some of these compounds are novel as they cannot be categorised in usual terms as carbohydrates, lipids, terpenes, steroids, proteins. Many of the biologically active compounds isolated are halogenated. Whereas metabolites containing iodine and chlorine are rarely found in terrestrial species, chlorinated, brominated, and iodinated compounds are widespread in marine fauna and flora. This suggests that many organisms have the ability to metabolise halide ions from the oceans (Yorke, 1977 and references therein).

Some genera of the red algae (Rhodophyta) have generated the most interest, partly because their species incorporate halogens into compounds with widely varying molecular weights. Species of the Laurencia genus of the Rhodomelaceae family dominate the list of red algae in which halogenated compounds have been found.

Locally, natural products from red algae are being investigated by Dr. M.H.G. Munro and co-workers. One of the

species they have investigated is Laurencia thyrsifera (Hook). From seaweed collected from the intertidal zone at Seal Reef, Kaikoura, New Zealand, an ether soluble oil was extracted and analysed. The compound known as thyrsiferyl acetate was the high molecular weight fraction isolated as an acetate derivative from the mixture eluted with polar solvents. It was found to be biologically inactive (Yorke, 1977).*

The molecular formula of thyrsiferyl acetate was determined as $C_{32}H_{55}O_8Br$ from high resolution mass spectra. From extensive pmr and ^{13}C nmr studies it was deduced to contain carbon atoms in the following environments: 11 quaternary methyl, 11 carbinol, 1 carbonyl and 1 halogenated. From the number of carbinol carbon atoms and the number of oxygen atoms known to be in the molecule, it was deduced that the compound contained four ether linkages and three hydroxyl groups, one of which was acetylated. Further, it was thought that the acetate group was in a secondary carbon environment and that one or more of these hydroxyl groups were attached to tertiary carbon atoms. Common structural features of the molecule were deduced to be:



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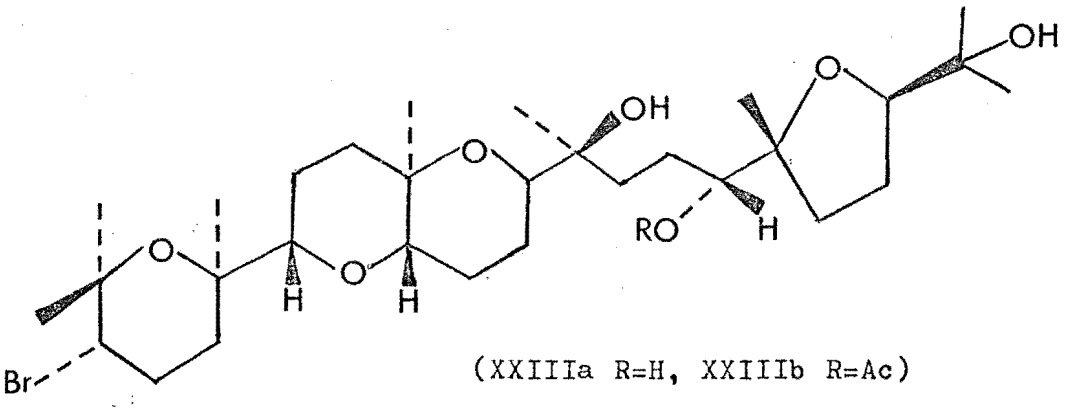
* The assay for biological activity was aimed at anti-fungal, antibacterial and antiyeast properties. The organic extract was tested on cultures grown in an agar medium.

Thus Munro and co-workers concluded they had isolated a novel compound which was a saturated, mono-brominated tetracyclic ether. The X-ray structure analysis described below has established thyrsiferyl acetate as (XXIIIb) and therefore, the parent alcohol thyrsiferol, is (XXIIIa). A report of



(XXIIIa R=H, XXIIIb R=Ac)

the structure has been submitted for publication to 'Tetrahedron Letters' (Blunt, Hartshorn, McLennan, Munro, Robinson and Yorke, 1977).

6.2 EXPERIMENTAL

The crystals used in this investigation were kindly supplied by Dr. M.H.G. Munro. Details of their preparation have been described elsewhere (Yorke, 1977; Blunt et al., 1977).

Preliminary investigations of the colourless crystals, using precession photography, showed them to be monoclinic with the condition limiting possible reflections (0k0, k=2n) consistent with space groups $P2_1$ or $P2_1/m$. The compounds known optical activity suggested the correct space group must be $P2_1$. This assignment was later confirmed by the successful solution and refinement of the structure. The size, shape

and mosaicity of the crystals meant they were only of marginal quality for diffractometry, but it was decided to continue the investigation.

The intensity data were collected using nickel-filtered CuKα X-radiation. The best crystal available was twinned but with a mosaicity of less than 0.5°. As the automatic centring procedure (Section 2.1.2) 'centred' the reflections approximately in the middle of the two peaks observed from ω-scans, no special procedures were adopted in the setting-up stage for automatic data collection. It was noted that in certain regions of reciprocal space (for low magnitude h and high magnitude k and l) high background counts, indicative of poor crystal centring, were obtained. The intensity data collection was proceeded with, however. Crystal and experimental data are given in Tables 6.1 and 6.2.

In the data reduction process intensities were corrected for Lorentz and polarisation effects but not for absorption. Some slight fluctuations in the intensities of the three standard reflections, monitored throughout the data collection were noted, but not corrected for. Their origin was probably some machine malfunction rather than crystal movement or decomposition.

6.3 SOLUTION AND REFINEMENT OF THE STRUCTURE

A Patterson synthesis was computed using all reflection data to determine the bromine atom position. The absence of Harker peaks corresponding to any mirror plane

Table 6.1

Crystal Data for $C_{32}H_{55}O_8Br$

Formula	$C_{32}H_{55}O_8Br$
Formula weight	647.69
System	Monoclinic
Space group	$P2_1$
a	12.348(4)Å
b	12.055(5)Å
c	12.166(5)Å
β	107.31(4)°
V	1728.93Å^3
D_{calc}	1.24 g cm^{-3}
Z	2
F(0,0,0)	692
μ(CuKα)	21.53 cm^{-1}

Table 6.2

Experimental Parameters for $C_{32}H_{55}O_8Br$

Crystal Dimensions	0.250 x 0.075 x .063 mm^3
Mosaicity	0.36 - 0.48°
θ scan range	1°
Scan time	50 secs.
Total background time	25 secs.
θ limit	50°
Total independent reflections	1931
Reflections used in refinements	1103 for which $F_o^2 \geq 3\sigma(F_o^2)$
Weighting parameter p	0.105
Ratio of observations to parameters	6.5

confirmed the space group as $P2_1$ with two molecules in the unit cell. A structure factor calculation including only one bromine atom, following two cycles of refinement of only the scale factor, yielded

$$R_1 = 0.402 \quad \text{and}$$
$$R_2 = 0.468.$$

These structure factors were input to a first difference Fourier synthesis. The choice of bromine co-ordinates (0.244, 0.25, 0.021), where the y value was deliberately chosen so that the screw related atom was located at y = 0.75 (co-ordinates: -0.244, 0.75, -0.021), highlighted a problem. These two bromine atoms appear to be related by a centre of symmetry on the screw axis at (0, 0.5, 0). As a result the calculated structure factors appeared as those of a centro-symmetric space group, i.e. with phases of 0 or π. Thus, the difference Fourier synthesis contained peaks not only for the true structure but also for its mirror image. The peaks of this map, apart from those on or very near the false mirror plane at y = 0.25, appeared in pairs at positions (x,y,z) and (x, 0.5 - y, z).

Three peaks that appeared, from distance and angle calculations, to correspond to three atoms of a six-membered ring were incorporated in a least-squares refinement - difference Fourier synthesis cycle. In this, and subsequent refinements, the y co-ordinate of the bromine atom was fixed to establish the origin. The incorporation of these three atoms into the model seemed to remove the peaks in the maps corresponding to the mirror image structure. After a further

series of refinement-difference Fourier cycles the R-factors were

$$R_1 = 0.236 \quad \text{and}$$
$$R_2 = 0.264 .$$

The model now contained the bromine atom, five oxygen atoms and 30 other atoms that were being refined as carbon atoms. At this stage there were several problems with the model; some temperature factors kept on decreasing while others, of atoms in chemically sensible positions, increased. Further the model consisted of two separate fragments. The larger fragment contained the bromine atom and the three six-membered ether rings. The disturbing feature of the other fragment, which included the three atoms extracted from the original difference Fourier synthesis, was the continued appearance of two triangular arrangements of atoms. A difference Fourier synthesis following a structure factor calculation containing only the 21 atoms of the larger fragment highlighted the problem with the earlier model. One of the three atoms originally used to separate the mirror related images did not belong to the same image as the other two. From this point the remaining atomic positions were slowly extracted from further difference Fourier syntheses. (A total of ten difference Fourier syntheses were necessary to find all the non-hydrogen atoms.) Difficulties occurred in establishing some of the terminal methyl group atoms as well as the acetate group. Further, the closest contact between the two fragments, initially very long (2.1Å), eventually became more chemically sensible (1.76(6)Å).

Refinements of this model, with all non-hydrogen atoms incorporated but with anisotropic thermal parameters for the bromine atom only, converged at

$$R_1 = 0.147 \quad \text{and}$$
$$R_2 = 0.165.$$

An attempt to discover the correct enantiomer was inconclusive at this stage. These calculations suggested an error in the weighting scheme and an analysis of the structure factors showed this to be so. The data were reprocessed using a p-factor of 0.105 (the original p-factor was 0.05) and the model was refined further to

$$R_1 = 0.144 \quad \text{and}$$
$$R_2 = 0.182.$$

A structure factor calculation for a model of opposite chirality gave

$$R_1 = 0.144 \quad \text{and}$$
$$R_2 = 0.183.$$

The function being minimised ($\Sigma w(|F_o|-|F_c|)^2$) had values for the two models of 6514 and 6569, respectively. Further, there were no significant differences in the bond distances and angles of the models. It was reluctantly concluded that with this poor quality data it was not really possible to establish the chirality using the anomalous scattering of the bromine atom. The 'centrosymmetric' position of the bromine atom is undoubtedly a contributing factor here also.

It was decided, partly for financial reasons, to

terminate refinement at this stage. The final structure factors are listed in Appendix 5. The largest shift in the final refinement cycle was 0.30σ and the mean shift was 0.11σ. The standard error in an observation of unit weight was 2.6. The minimised function showed little systematic dependence on either $|F_o|$ or $\sin\theta$. A structure factor calculation using all data revealed no anomalies and gave

$$R_1 = 0.238 \quad \text{and}$$
$$R_2 = 0.199.$$

The peaks of highest magnitude (at about $\pm 1 e\text{Å}^{-3}$) in a final difference Fourier synthesis were clustered about the bromine atom position. There were no strong indications of hydrogen atom positions.

Final positional and thermal parameters are given in Table 6.3.

6.4 DESCRIPTION OF THE STRUCTURE

Two views, related by a 90° rotation, of a molecule of thyrsiferyl acetate are shown in Figure 6.1. The labelling scheme was chosen to show up the long chain of 24 carbon atoms in the molecule. Interatomic distances and bond angles are given in Tables 6.4 and 6.5.

The conformations of two of the six-membered rings (Rings (1) and (2) in Figure 6.1) are chairs, whereas the other, Ring (3), is in a twist-boat conformation. Displacements of the individual atoms from the mean-planes through each of the rings are given in Table 6.6. In Ring (1) the

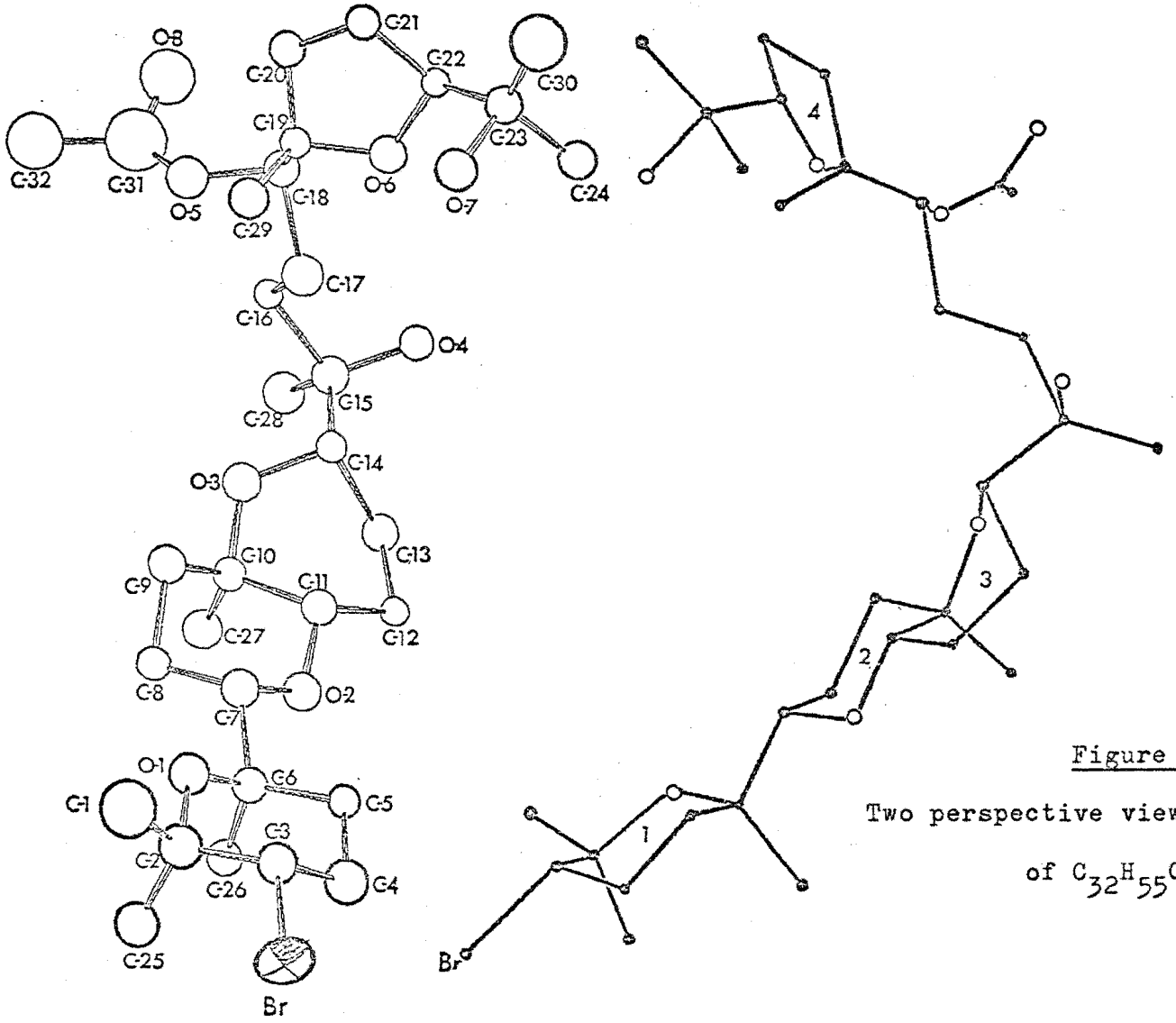


Figure 6.1

Two perspective views of one molecule of $C_{32}H_{55}O_8Br$

Table 6.3(a)

Positional Parameters ($x10^3$, except for Br which is $x10^4$) and Isotropic Thermal Parameters (x10) for $C_{32}H_{55}O_8Br$

	x	y	z	
Br	2389(4)	2500	263(5)	
O(1)	517(2)	438(2)	232(2)	6.0(9)
O(2)	540(2)	734(3)	249(2)	5.7(9)
O(3)	818(2)	874(3)	346(2)	6.1(9)
O(4)	855(2)	1133(2)	204(2)	4.9(8)
O(5)	1185(3)	879(3)	274(3)	7(1)
O(6)	1067(2)	934(2)	-14(2)	5.6(9)
O(7)	991(2)	807(3)	-218(2)	6.3(9)
O(8)	1314(4)	1000(4)	349(4)	12(1)
C(1)	511(5)	240(7)	186(5)	11(2)
C(2)	441(4)	334(4)	199(4)	6(1)
C(3)	354(3)	366(4)	80(4)	6(1)
C(4)	292(4)	484(4)	75(4)	7(1)
C(5)	383(3)	571(3)	108(3)	4(1)
C(6)	467(3)	549(4)	232(4)	5(1)
C(7)	582(4)	615(4)	249(4)	6(1)
C(8)	671(3)	602(3)	363(4)	5(1)
C(9)	774(4)	687(4)	357(4)	6(1)
C(10)	725(3)	803(4)	357(4)	4(1)
C(11)	625(4)	809(4)	237(4)	5(1)
C(12)	572(3)	928(3)	216(3)	4(1)
C(13)	672(4)	1014(4)	265(4)	7(1)
C(14)	796(3)	958(4)	252(3)	4(1)
C(15)	879(4)	1062(4)	300(4)	6(1)
C(16)	1007(3)	996(3)	302(3)	3(1)

Table 6.3 contd.

	x	y	z	
C(17)	1000(4)	944(4)	195(4)	6(1)
C(18)	1129(4)	943(4)	171(4)	5(1)
C(19)	1143(3)	884(3)	87(3)	4(1)
C(20)	1249(3)	886(4)	52(3)	5(1)
C(21)	1223(3)	891(4)	-79(3)	4(1)
C(22)	1109(3)	949(3)	-116(3)	3(1)
C(23)	1033(4)	922(4)	-236(4)	5(1)
C(24)	1073(5)	902(6)	-339(5)	11(2)
C(25)	389(4)	312(4)	291(4)	7(1)
C(26)	412(3)	572(4)	328(4)	5(1)
C(27)	688(4)	831(4)	453(4)	6(1)
C(28)	897(4)	1112(4)	425(4)	7(1)
C(29)	1109(3)	741(5)	75(3)	6(1)
C(30)	926(4)	999(4)	-260(4)	5(1)
C(31)	1264(7)	913(8)	364(7)	15(2)
C(32)	1332(5)	845(6)	468(6)	12(2)

Table 6.3(b)

Anisotropic Thermal Parameters ($x10^3$ for Br)

U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
69(3)	44(3)	119(5)	-40(3)	13(3)	-34(4)

Table 6.4

Interatomic Distances(Å) in $C_{32}H_{55}O_8Br$

Br-C(3)	1.96(4)	C(6)-C(26)	1.54(6)
		C(7)-C(8)	1.49(5)
O(1)-C(2)	1.54(5)	C(8)-C(9)	1.65(6)
O(1)-C(6)	1.48(5)	C(9)-C(10)	1.53(6)
O(2)-C(7)	1.52(5)	C(10)-C(11)	1.60(5)
O(2)-C(11)	1.42(5)	C(10)-C(27)	1.42(5)
O(3)-C(10)	1.47(5)	C(11)-C(12)	1.56(6)
O(3)-C(14)	1.49(4)	C(12)-C(13)	1.58(6)
O(4)-C(15)	1.41(5)	C(13)-C(14)	1.72(6)
O(5)-C(18)	1.46(5)	C(14)-C(15)	1.61(6)
O(5)-C(31)	1.29(8)	C(15)-C(16)	1.76(6)
O(6)-C(19)	1.44(4)	C(15)-C(28)	1.60(6)
O(6)-C(22)	1.49(4)	C(16)-C(17)	1.43(6)
O(7)-C(23)	1.52(5)	C(17)-C(18)	1.71(6)
		C(18)-C(19)	1.30(5)
O(8)-C(31)	1.25(8)	C(19)-C(20)	1.48(5)
		C(19)-C(29)	1.78(7)
C(1)-C(2)	1.47(7)	C(20)-C(21)	1.54(5)
C(2)-C(3)	1.57(6)	C(21)-C(22)	1.51(5)
C(2)-C(25)	1.47(6)	C(22)-C(23)	1.51(5)
C(3)-C(4)	1.60(6)	C(23)-C(24)	1.50(7)
C(4)-C(5)	1.50(6)	C(23)-C(30)	1.58(6)
C(5)-C(6)	1.58(5)	C(31)-C(32)	1.54(8)
C(6)-C(7)	1.58(6)		

Table 6.5

Bond Angles (°) in $C_{32}H_{55}O_8Br$

C(2)-O(1)-C(6)	121(3)	C(8)-C(9)-C(10)	105(3)
C(7)-O(2)-C(11)	110(3)	O(3)-C(10)-C(9)	102(3)
C(10)-O(3)-C(14)	119(3)	O(3)-C(10)-C(11)	108(3)
C(18)-O(5)-C(31)	127(5)	O(3)-C(10)-C(27)	113(4)
C(19)-O(6)-C(22)	117(3)	C(9)-C(10)-C(11)	104(4)
		C(9)-C(10)-C(27)	117(4)
O(1)-C(2)-C(1)	109(4)	C(11)-C(10)-C(27)	113(4)
O(1)-C(2)-C(3)	103(4)	O(2)-C(11)-C(10)	106(3)
O(1)-C(2)-C(25)	109(4)	O(2)-C(11)-C(12)	109(3)
C(1)-C(2)-C(3)	111(4)	C(10)-C(11)-C(12)	111(3)
C(1)-C(2)-C(25)	110(5)	C(11)-C(12)-C(13)	107(3)
C(3)-C(2)-C(25)	115(4)	C(12)-C(13)-C(14)	109(3)
Br-C(3)-C(2)	111(3)	O(3)-C(14)-C(13)	99(3)
Br-C(3)-C(4)	109(3)	O(3)-C(14)-C(15)	107(3)
C(2)-C(3)-C(4)	116(3)	C(13)-C(14)-C(15)	99(3)
C(3)-C(4)-C(5)	107(3)	O(4)-C(15)-C(14)	103(3)
C(4)-C(5)-C(6)	112(3)	O(4)-C(15)-C(16)	105(3)
O(1)-C(6)-C(5)	107(3)	O(4)-C(15)-C(28)	120(4)
O(1)-C(6)-C(7)	96(3)	C(14)-C(15)-C(16)	98(3)
O(1)-C(6)-C(26)	116(4)	C(14)-C(15)-C(28)	122(4)
C(5)-C(6)-C(7)	111(3)	C(16)-C(15)-C(28)	106(3)
C(5)-C(6)-C(26)	112(3)	C(15)-C(16)-C(17)	111(3)
C(7)-C(6)-C(26)	113(3)	C(16)-C(17)-C(18)	111(4)
O(2)-C(7)-C(6)	101(3)	O(5)-C(18)-C(17)	95(3)
O(2)-C(7)-C(8)	105(3)	O(5)-C(18)-C(19)	104(4)
C(6)-C(7)-C(8)	117(4)	C(17)-C(18)-C(19)	120(4)
C(7)-C(8)-C(9)	105(4)	O(6)-C(19)-C(18)	104(4)

Table 6.5 contd.

O(6)-C(19)-C(20)	99(3)	O(7)-C(23)-C(22)	101(3)
O(6)-C(19)-C(29)	104(3)	O(7)-C(23)-C(24)	101(4)
C(18)-C(19)-C(20)	124(4)	O(7)-C(23)-C(30)	105(3)
C(18)-C(19)-C(29)	121(4)	C(22)-C(23)-C(24)	125(4)
C(20)-C(19)-C(29)	102(3)	C(22)-C(23)-C(30)	108(3)
C(19)-C(20)-C(21)	112(3)	C(24)-C(23)-C(30)	114(4)
C(20)-C(21)-C(22)	103(3)	O(5)-C(31)-O(8)	116(8)
O(6)-C(22)-C(21)	103(3)	O(5)-C(31)-C(32)	128(8)
O(6)-C(22)-C(23)	120(3)	O(8)-C(31)-C(32)	113(7)
C(21)-C(22)-C(23)	116(6)		

Table 6.6

Least-squares Planes of $C_{32}H_{55}O_8Br$

(a) Atoms defining planes and distances of atoms from planes (Å)

plane (1)		plane (2)		plane (3)		plane (4)	
O(1)	0.21(3)	O(2)	-0.29(3)	O(3)	-0.10(3)	O(6)	-0.01(3)
C(2)	-0.20(5)	C(7)	0.28(5)	C(10)	-0.39(4)	C(19)	0.10(4)
C(3)	0.23(4)	C(8)	-0.30(4)	C(11)	0.46(4)	C(20)	-0.16(4)
C(4)	-0.27(5)	C(9)	0.32(5)	C(12)	-0.03(4)	C(21)	0.14(4)
C(5)	0.26(4)	C(10)	-0.31(4)	C(13)	-0.46(4)	C(22)	-0.08(4)
C(6)	-0.23(4)	C(11)	0.29(4)	C(14)	0.52(4)		

(b) Interplanar angles (°)

1 - 2	17.2	1 - 3	32.1	1 - 4	92.0
2 - 3	15.0	2 - 4	76.4	3 - 4	63.6

bromine atom is, as expected, an equatorial substituent. It is displaced by -0.334(6)Å from the mean-plane of the ring. There is a 1,3-diaxial interaction between the C(2)-C(25) and C(6)-C(26) bonds. The C(25)-C(26) distance, however, is 3.17Å and is not particularly short. It is not surprising to find a twist-boat conformation for Ring (3) because if it were a chair arrangement, there would be a 1,3-parallel interaction between the C(10)-C(27) bond, which must be in an axial position, and the C(14)-C(15) bond.

In the five-membered ring Ring (4) the oxygen atom lies on the mean-plane with the remaining atoms lying alternately above and below this plane (Table 6.6).

An examination of non-bonded distances reveals that O(4)...O(7'), at 2.80(4)Å, is the only intermolecular contact not involving hydrogen atoms less than 3.4Å. This is within the range 2.55-2.96 (mean value 2.74)Å quoted for the separation of oxygen atoms where hydrogen bonding occurs in alcohols (Pimentel and McClellan, 1960). It is very much less than the corresponding Van der Waal's contact distance of 3.04Å (Bondi, 1964). The packing of molecules is believed to be dominated by hydrogen bonding of this type. Each molecule is linked to two others, related to it by a single screw axis, resulting in the formation of columns of hydrogen bonded molecules, parallel to the b-axis of the cell and the longest dimension of the molecules. One such chain is shown in Figure 6.2.

The O(7)...O(6) intramolecular distance at 2.84(Å) is also short. This is possibly indicative of a further hydrogen bond resulting in the formation of a five-membered

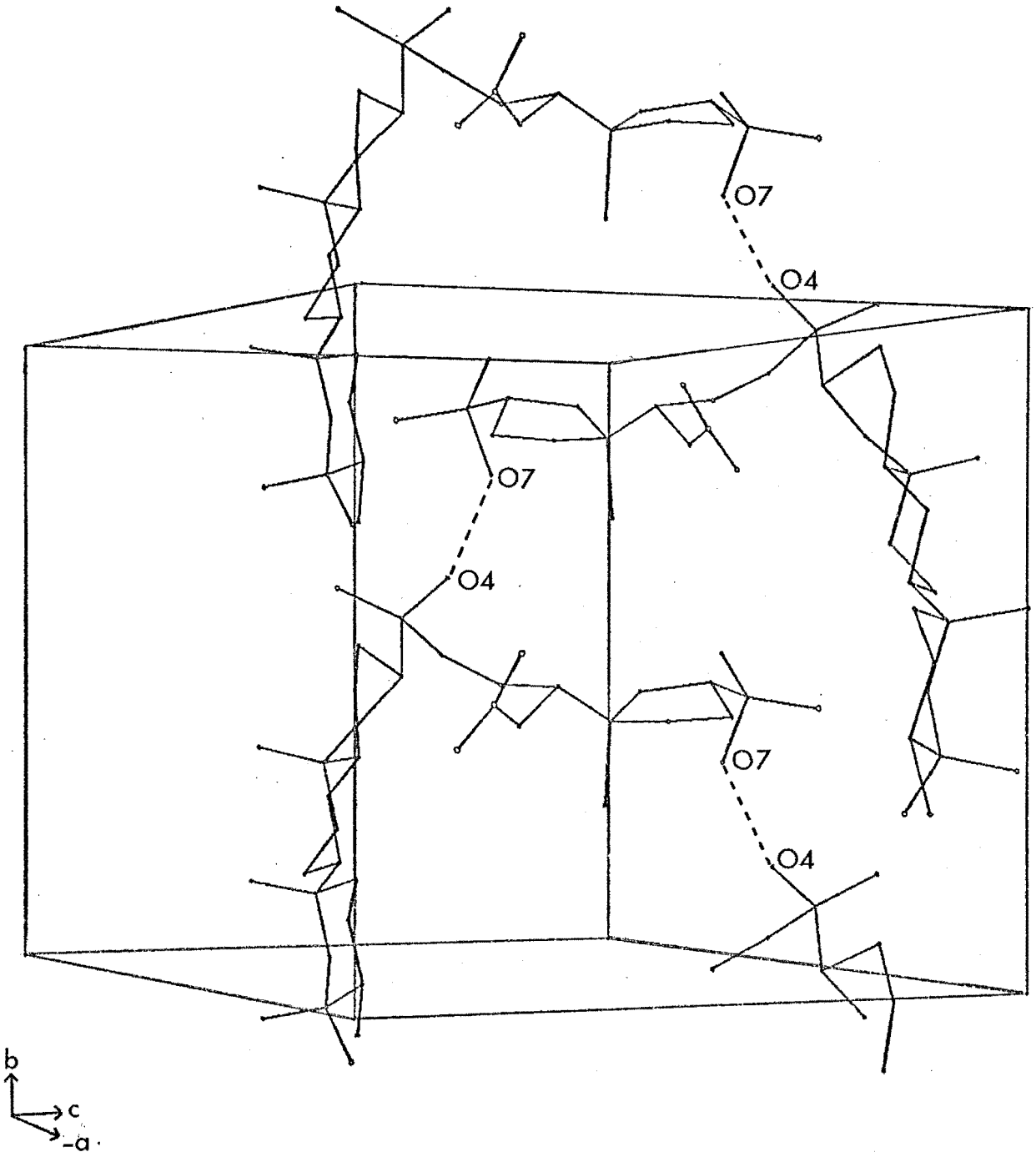


Figure 6.2

Packing of molecules of $C_{32}H_{55}O_8Br$

A single column of hydrogen bonded molecules is shown.

ring (O(6), C(22), C(23), O(7) and the hydrogen atom attached to O(7)). Such a bond would be very bent (the O-H...O angle has been calculated as approximately 120°) and certainly not strong. Very bent intramolecular O-H...O hydrogen bonds have been proposed elsewhere (e.g. 143° (Gupta and Yadav, 1974); 114° (Holloway, Pannell and Penfold, 1975)). A possible hydrogen bonding scheme for thyrsiferyl acetate is:- O(4')-H'...O(7), O(7)-H...O(6), and O(4)-H...O(7"), where the unprimed atoms are all in one molecule. The exact nature of hydrogen bonding cannot be established without the location of hydrogen atom positions and this was not possible in this analysis.

There were no other unusually short intramolecular contacts.

6.5 DISCUSSION

The structure determination of thyrsiferyl acetate has been successful in that the relative configuration of the molecule, if not the absolute configuration, has been established beyond doubt. The poor quality of the crystal from which the data were collected, and the limited number of parameters of the structural model, have resulted in an analysis of very limited accuracy. Within these limitations there are no remarkable features in the bond distances and angles other than the two short oxygen-oxygen contacts.

In a single aspect the structure is at variance with the description obtained from the nmr studies. From these it had been deduced that there were 11 methyl groups in the

molecule but in fact there are only 9. Thyrsiferyl acetate can be considered to be an isoprenoid compound, consisting of six isoprene units (Figure 6.3). The compound is formally a derivative of the acyclic terpene, squalene ($C_{30}H_{50}$). The other two carbon atoms in the formula $C_{32}H_{55}O_8Br$ belong to the acetate group.

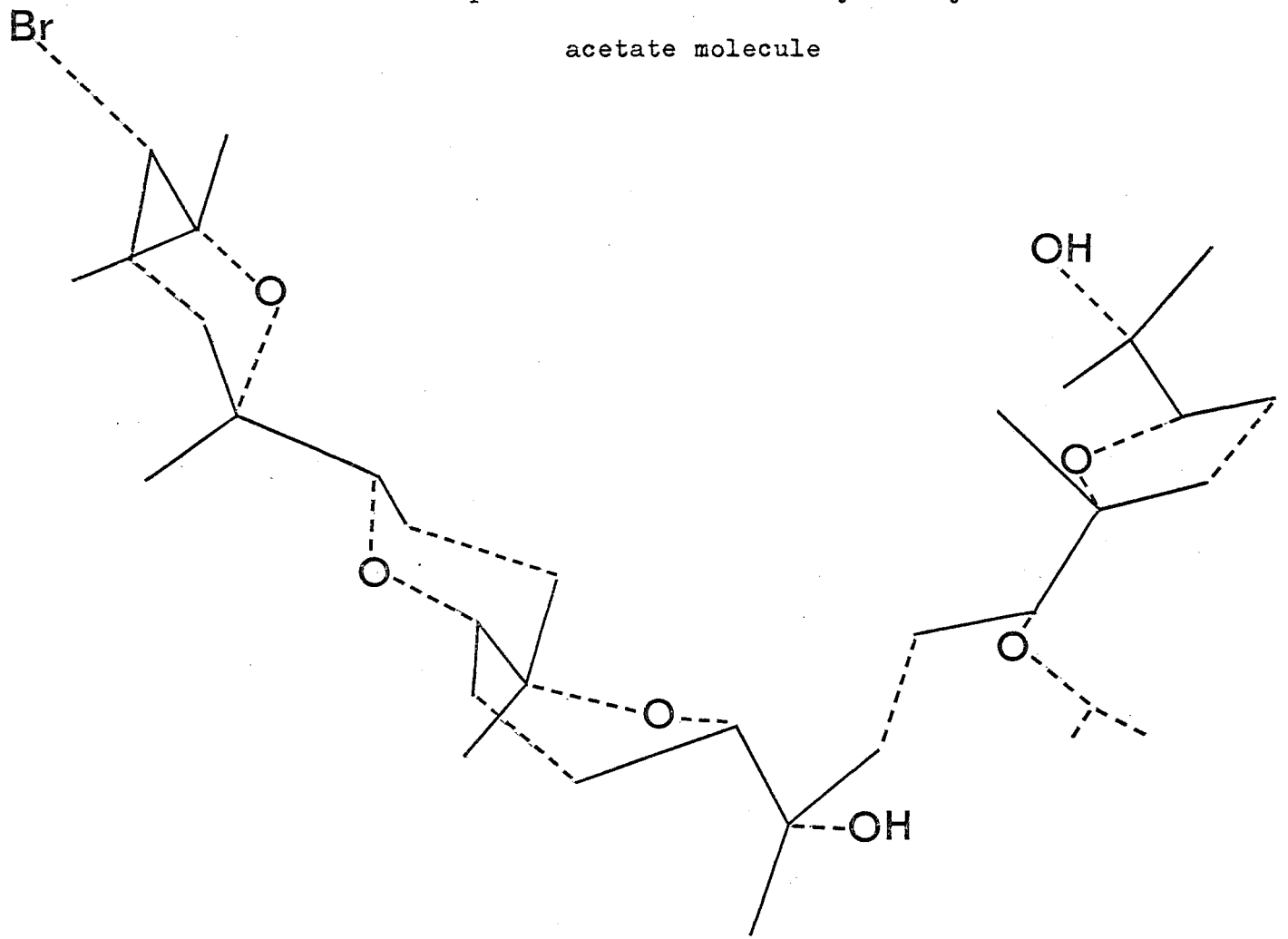
Previous investigations of red algae of the genus Laurencia have established the structures of many interesting metabolites based in the main on fatty acid, sesquiterpenoid, or diterpenoid skeletons (Faulkner, 1977; Fenical, 1975). Thyrsiferol appears to be the first metabolite related to squalene to be isolated and identified from a Laurencia species.

Postscript (23rd January, 1978)

The paper entitled 'Thyrsiferol: A Squalene-derived Metabolite of Laurencia Thyrsifera' (Blunt, Hartshorn, McLennan, Munro, Robinson and Yorke, 1977) has recently been published (Tetrahedron Letters, 1978, 69 (1978)).

Figure 6.3

Isoprenoid units in the thyrsiferyl acetate molecule



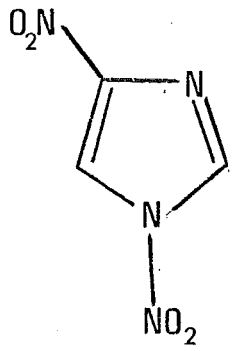
CHAPTER 7

UNSUCCESSFUL STRUCTURE ANALYSES

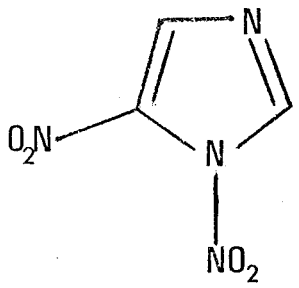
7.1 STRUCTURAL STUDY OF A DINITROIMIDAZOLE DERIVATIVE

7.1.1 Introduction

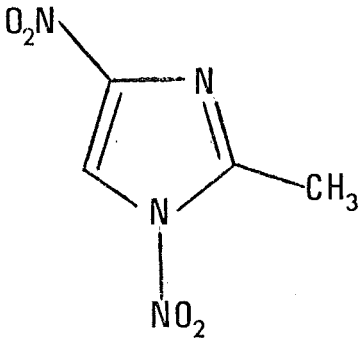
In the course of synthetic studies Dr. Ross Grimmett, of Otago University, has prepared an imidazole derivative which he has not been able to identify. It is either 1,4-dinitroimidazole (XXIV) or 1,5-dinitroimidazole (XXV). This particular product is not suitable for crystal structure analysis but its 2-methyl derivative ((XXVI) or (XXVII)) is.



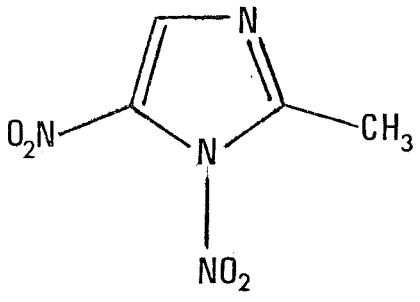
(XXIV)



(XXV)



(XXVI)



(XXVII)

Dr. M. Claire Couldwell collected the intensity data in this laboratory and she attempted to solve the structure by Patterson synthesis methods. Both two- and three-dimensional maps were studied. These efforts were unsuccessful and the data were given to this author who made further attempts to solve the structure using direct methods.

7.1.2 Experimental

Dr. M.C. Couldwell collected the data from crystals supplied by Dr. R. Grimmett. Her preliminary investigation using precession photography of the colourless crystals showed the space group to be $P2_12_12_1$ (conditions limiting possible reflections were hOO for h = 2n, OkO for k = 2n and OOl for l = 2n). The crystal data are given in Table 7.1.

As the crystals appeared to crumble during exposure to X-radiation, the crystal used for data collection was fixed to the inside of a pyrex capilliary. The intensity data were collected using zirconium-filtered MoKα radiation. The parameters used in the data collection are given in Table 7.2. Corrections for slight crystal decomposition (about 3% over the course of the entire experiment) were applied as part of the data reduction process. The intensities were not corrected for absorption.

7.1.3 Attempted Structure Solution by Direct Methods

The first attempts to solve this structure by direct methods used the 1971 version of program MULTAN. The initial generation of normalised structure factors using program SH.NORM highlighted an undesirable feature of the data. The overall temperature factor, extracted from a Wilson plot of

Table 7.1

Crystal Data for $C_3HN_2(NO_2)_2CH_3$

Formula	$C_4N_4O_4H_4$
Formula weight	172.10
System	Orthorhombic
Space group	$P2_12_12_1$
a	8.094(1)Å
b	14.482(3)Å
c	6.023(1)Å
V	706.0Å^3
D_{calc}	1.62 g cm^{-3}
D_{meas}	1.59 g cm^{-3}
Z	4
F(0,0,0)	352
μ(MoKα)	1.57 cm^{-1}

Table 7.2

Experimental Parameters for $C_3HN_2(NO_2)_2CH_3$

Crystal dimensions	0.06 x 0.06 x 0.12mm^3
Mosaicity	0.12 - 0.18°
Θ scan range	0.60°
Scan time	60 sec.
Total background time	30 sec.
Θ limit	24°
Total independent reflections	676
Reflections for which $F_o^2 \geq 3\sigma(F_o^2)$	68

all data (Wilson, 1942), was negative. A more reasonable value was obtained by using only those reflections for which $\theta < 19^{\circ}$ in the Wilson plot. 164 normalised structure factors ($|E| \geq 1.3$) were generated and used as input to program MULTAN. None of the E-maps synthesised from the resulting phase sets could be satisfactorily interpreted.

Following the implementation of the MULTAN74 package of programs (Main, Woolfson, Lessinger, Germain and Declercq, 1974) at the University of Canterbury, which will be described in the following chapter, further attempts were made to solve this structure. The program NORMAL, which as part of this suite is used to generate $|E|$'s, is much more flexible than program SHNORM. It is possible to normalise structure factors in their individual purity groups. In such cases, the convergence procedure used to find a suitable starting set for the tangent refinement of phases, is likely to proceed more smoothly. A further feature of program NORMAL is the facility for using molecular or group scattering factors in cases where the stereochemistry of the whole molecule, or at least part of the molecule, is known. i.e. A random distribution of atoms in the cell is no longer assumed. This is achieved by replacing f_j the scattering factor for the jth atom, in the formula for normalised structure factors, by the spherically average scattering factor of the jth group g_j, where

$$g_j^2 = \sum_{lk}^{mm} \frac{f_l f_k \sin(d_{lk} \cdot 4\pi \mathrm{Sin}\theta/\lambda)}{d_{lk}\, 4\pi \mathrm{Sin}\theta/\lambda}$$

and d_{lk} is the distance between the lth and kth atoms in the group and there are m atoms in the group. This feature helps remove the spurious peaks particularly common in the E-maps of planar molecules.

Several sets of |E|'s, scaled in individual parity groups, using parameters derived from the reduced set of reflections ($\theta < 19^{o}$) and incorporating a group scattering factor for the imidazole ring, were generated. The sets differed in size and different scale factors were applied. Subsequent origin definitions and tangent refinements of phases did not lead to the solution of the structure.

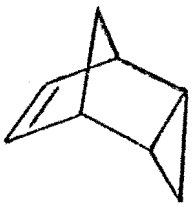
It is apparent that a better set of intensity data is required for a successful structure analysis. Apart from the negative overall temperature factor of this set, there were only 68 reflections for which $F_o^2 \geqslant 3\sigma(F_o^2)$. Unfortunately, the crystals diffract X-rays poorly but it should be possible to obtain better quality data with a change to copper radiation coupled with greater attention to experimental parameters. e.g. Care in the selection of incident and reflected X-ray beam collimators and the use of increased scan times should reduce the signal to noise ratio. The author understands that a recollection of the intensity data is planned in the near future.

7.2 STRUCTURAL STUDY OF COMPOUND WITH PROPOSED FORMULA 4,4,5,5-TETRACYANO-8-METHYLTETRACYCLO[4.2.2.$O^{2,8}$.$O^{3,10}$] DECANE

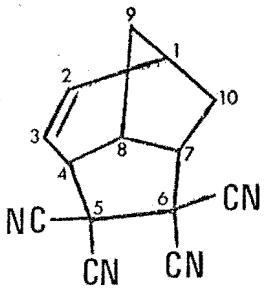
7.2.1 Introduction

The reaction of endo-tricyclo[3.2.1.$O^{2,4}$]oct-6-ene(XXVIII)

with TCNE in methylene chloride has been shown, by an X-ray structure analysis, to give 5,5,6,6-tetracyanotricyclo-[5.2.1.$0^{4,8}$]dec-2-ene (XXIX) (Battiste, Coxon, Posey, King, Mathew and Palenik, 1975).

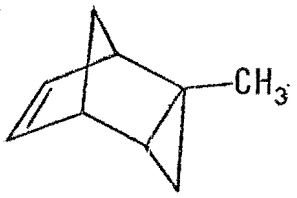


(XXVIII)

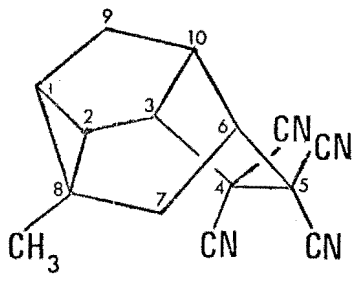


(XXIX)

Further studies at this university by Dr. J.M. Coxon and co-workers have been made of 2-exo-methyl-endo-tricyclo [3.2.1.$0^{2,4}$]oct-6-ene (XXX), which is prepared by the reaction of cyclopentadiene with 1-methylcyclopropene (Magid, Clarke and Duncan, 1971). This hydrocarbon reacts with TCNE in methylene chloride to give a compound shown from elemental analysis and the mass spectrum to be a 1:1 adduct. From ^{13}Cnmr and pmr studies the compound was deduced to be 4,4,5,5-tetracyano-8-methyltetracyclo[4.2.2.$0^{2,8}$.$0^{3,10}$]-decane (XXXI) (Coxon, de Bruijn and Lau, 1975). A X-ray structure analysis was undertaken to confirm this result but so far it has been unsuccessful.



(XXX)



(XXXI)

7.2.2 Experimental

Colourless, plate-shaped crystals were supplied by Dr. J.M. Coxon. A preliminary investigation by precession photography indicated the space-group to be $P2_1/C$ (conditions limiting possible reflections: OkO, k=2n; hOl, l=2n). Crystal data are listed in Table 7.3. The experimental density corresponded, surprisingly, to 12 molecules of $C_{15}H_{12}N_4$ in the unit cell. No peak was found in the mass spectrum of the crystal used for the preliminary study, for a species of higher mass and no evidence could be found for the incorporation of solvent in the crystal lattice. It was concluded that the asymmetric unit includes electron density equivalent to three empirical formulas.

Many crystals were examined and found to be twinned before one suitable for diffractometry was found. The intensity data were collected using nickel-filtered CuKα radiation. Details of the experiment are given in Table 7.4. Standard data collection and reduction procedures were used. Linear corrections for a crystal decomposition of 10% during the course of the data collection but not for absorption were applied.

7.2.3 Attempted Structure Solution

The application of direct methods is the only path likely to lead to the successful solution of this structure. On the basis of three molecules in the asymmetric unit there are 57 non-hydrogen atoms to be located. Previous experience in this laboratory has shown that crystal structure solution of light atom problems, crystallising in centro-

Table 7.3

Crystal Data for $C_{15}H_{12}N_4$

Proposed Formula	$C_{15}H_{12}N_4$
Formula weight	248.29
System	Monoclinic
Space group	$P2_1/c$
a	23.689(3)Å
b	13.235(2)Å
c	12.414(2)Å
β	97.74(1)°
V	3856.8Å^3
D_{meas}	1.27 g cm^{-3}
D_{calc}	1.29 g cm^{-3}
Z	12
F(0,0,0)	1560
μ(CuKα)	6.48 cm^{-1}

Table 7.4

Experimental Parameters for $C_{15}H_{12}N_4$

Crystal dimensions	0.25 x 0.23 x 0.08 mm^3
Mosaicity	.21 - .36°
θ scan range	0.72°
Scan time	72 sec.
Total background time	36 sec.
θ limit	57°
Total independent reflections	5366
Reflections for which $F_o^2 \geq 3\sigma(F_o^2)$	2000

symmetric space groups, generally proceeds straightforwardly. In the relatively few cases in which the solution does not appear quickly a considerable length of time and a large number of program executions can precede the eventual emergence of the correct structure.

Three direct methods programs, from different authors, were used in the attempts to solve this structure:- MULTAN74, SAP (Hall, 1968) based on the NRC program for centrosymmetric space groups, and SHELX-76 (Sheldrick, 1975). A number of E-maps were examined and several models containing chemically reasonable molecular fragments were further explored by least-squares refinement and difference Fourier cycles. None of these models could be developed into a sensible structural model.

An obvious course to pursue was using molecular fragments to generate the starting phases for further tangent refinement. The program module which writes such a file for input into MULTAN74 was not as yet available, here. Initially, when the problem was thought to be a 19 atom structure it had been considered a very suitable one for testing concurrent program developments. As a 57 atom problem it was too large and the computing cost too high to be suitable for this purpose. It was decided, therefore, to leave this analysis in this unsatisfactory state and instead to undertake the thyrsiferyl acetate analysis described in the previous chapter.

CHAPTER 8

A REVIEW OF SOME OF THE RECENT CRYSTALLOGRAPHIC COMPUTER PROGRAM DEVELOPMENTS AT THE UNIVERSITY OF CANTERBURY

8.1 COMPUTER SYSTEM

Calculations during the structure analyses described earlier, except for diffractometer control, were in the main performed on a Burroughs B6718 computer although some initial data processing was carried out on an IBM 360/44 computer. The 360/44, at the time it was replaced, had 32K words (32 bits) of memory and 2 million bytes (8 bits) of disk storage. The limitations of this computer, and probably the local charging scheme, meant that the crystallographic programs had been highly optimised for this hardware and contained many machine dependent features. For example key routines in program CUCLS had been written in machine language to minimise execution times. Also, programs had considerable file blocking to reduce input/output times. Initial conversion of the programs to run on the B6718, after its arrival in 1973, took about a year and the efforts of several people.

The present configuration of the Burroughs B6718 (Figure 8.1) includes a single processor, 160K words (48 bits) of main memory and extensive disk storage capacity. Individual user files are mainly stored on magnetic tape although a limited disk area is available for permanent storage of crystallographic programs. All interactive terminals,

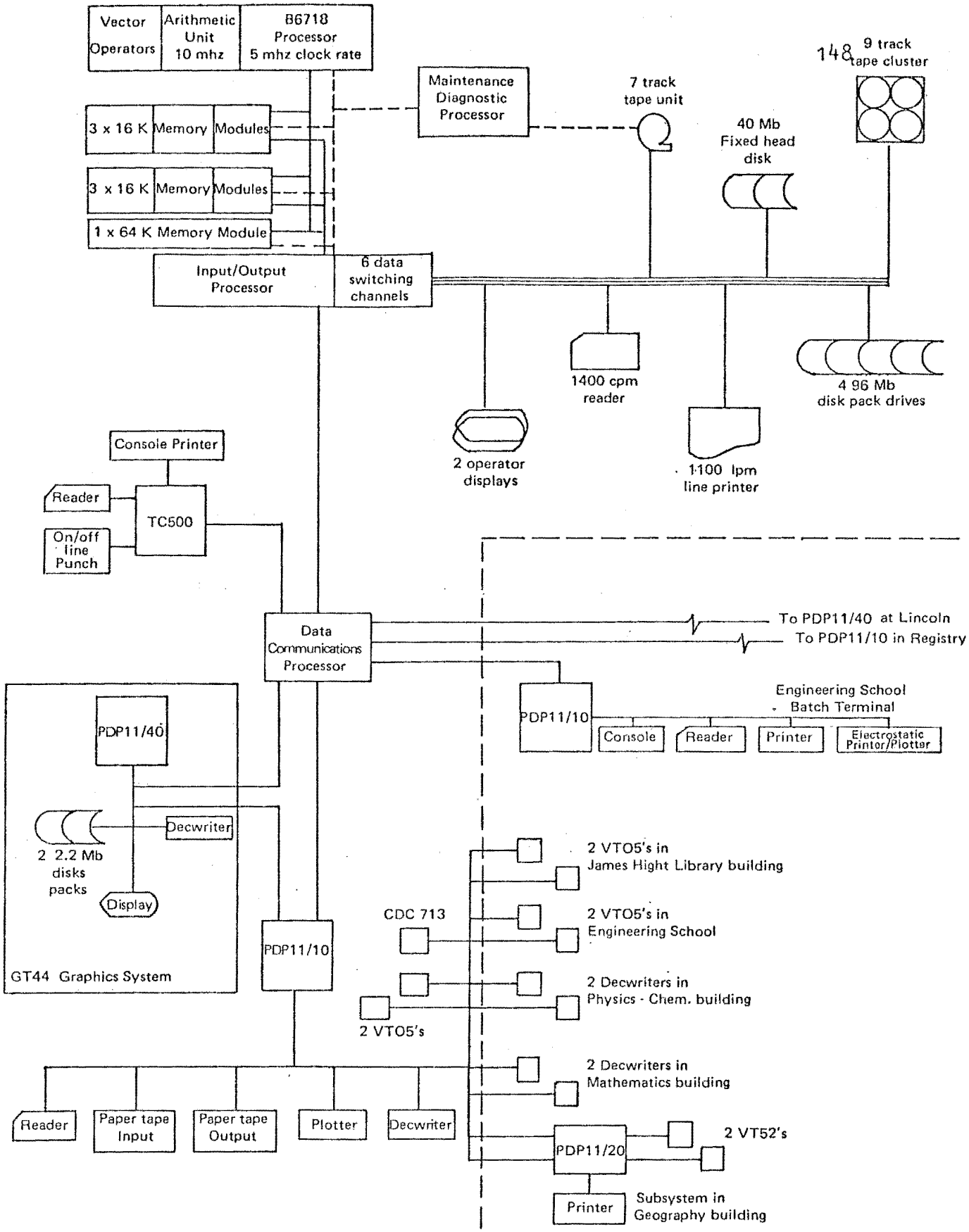


Figure 8.1

Schematic diagram of Computer Centre equipment

(reproduced with permission)

plotting on the CALCOMP plotter, and paper-tape processing are controlled by a DEC PDP11/10 computer interfaced to the data communications processor of the B6718. In addition to a batch terminal, there are 10 interactive terminals for general use. These are either of screen type (VT05'S) or printer type (Decwriter's). The DEC GT44 graphics system was not used in this project.

The architecture of the Burroughs B6700 computer series (Organick, 1973) was based on the novel design of the earlier B5500 series. The hardware and software were specially designed to cater for algorithms expressed in block-structured (i.e. nested declaration of program variables), recursive languages. The operating system is, in fact, written in an extension of Algol 60 (Naur, 1963) and there is no assembly language available to the user. Key features of the B6700 are the use of stacks to maintain current program descriptions and a 'virtual memory' system. Programs may, at least in theory, be of unlimited size rather than having to fit into a memory partition of fixed size typical of the operating systems for other multi-programming machines. Program code is segmented into blocks which are rarely all present in memory at a given stage in program execution. Those blocks currently not active are stored on disk. Storage for large arrays is usually handled in a similar manner, a feature which gave rise to many of the problems encountered initially.

From the point of view of machine efficiency there would be obvious advantages in programming in the language for which the machine was designed i.e. Burroughs Extended Algol. However, the 'portability' and the availability of

Fortran programs, have tended to restrict programming in Algol to tasks for which Fortran is particularly inappropriate e.g. character handling where bit manipulation is necessary.

8.2 X-RAY CRYSTALLOGRAPHIC PROGRAM LIBRARY

The major computer programs used for the solution and refinement of structures on the 360/44 and originally implemented on the B6718 are listed in Table 8.1. Small programs, used for purposes such as contouring electron density maps and calculating hydrogen atom positions or rigid-body parameters are not included in this table. Programs which are not discussed in Chapter 2 were based on others as follows:- DABS on DATAPH (Coppens and Hamilton, 1969), CORFFE on ORFFE (Busing, Martin and Levy, 1964), MEANPLANE on NRC-22 (Pippy and Ahmed, 1967), DANTEP on an earlier version of ORTEP (Johnson, 1965), and SUPERPOSITION on the package of Hubbard and Jacobsen (1969). Some details of the adaptation of these, and other programs, to the present program suite (Table 8.2), allowing for a very flexible approach to structure solution, are given in the sections below.

8.3 COMPUTER PROGRAMMING

The computer programming projects undertaken by the author can be broken into three categories:- the conversion of Fortran programs to the B6718, developments of the diffractometer control programs and the initial developments of an interactive system of crystallographic programs for the B6718.

Table 8.1

Crystallographic Computing System (1973)

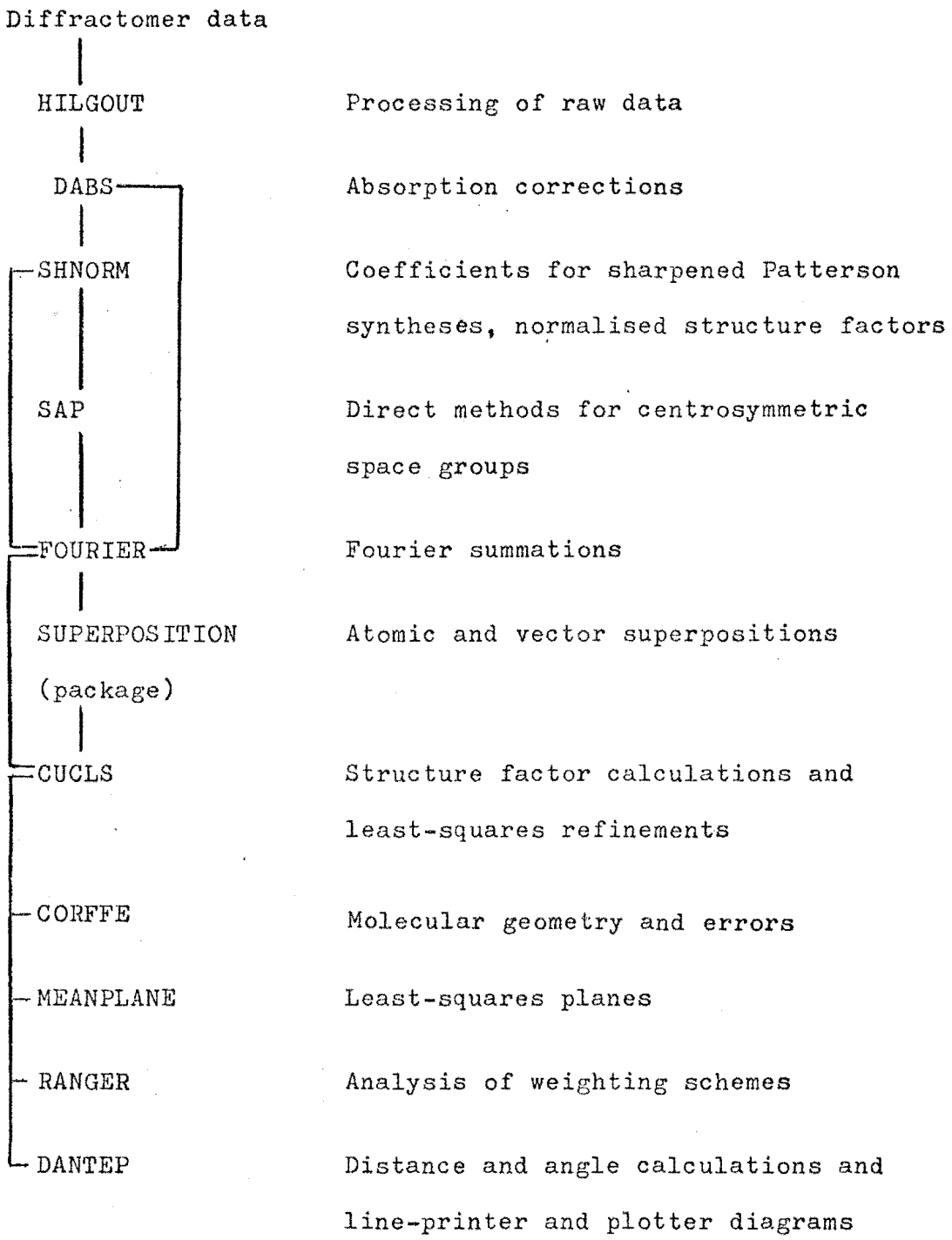
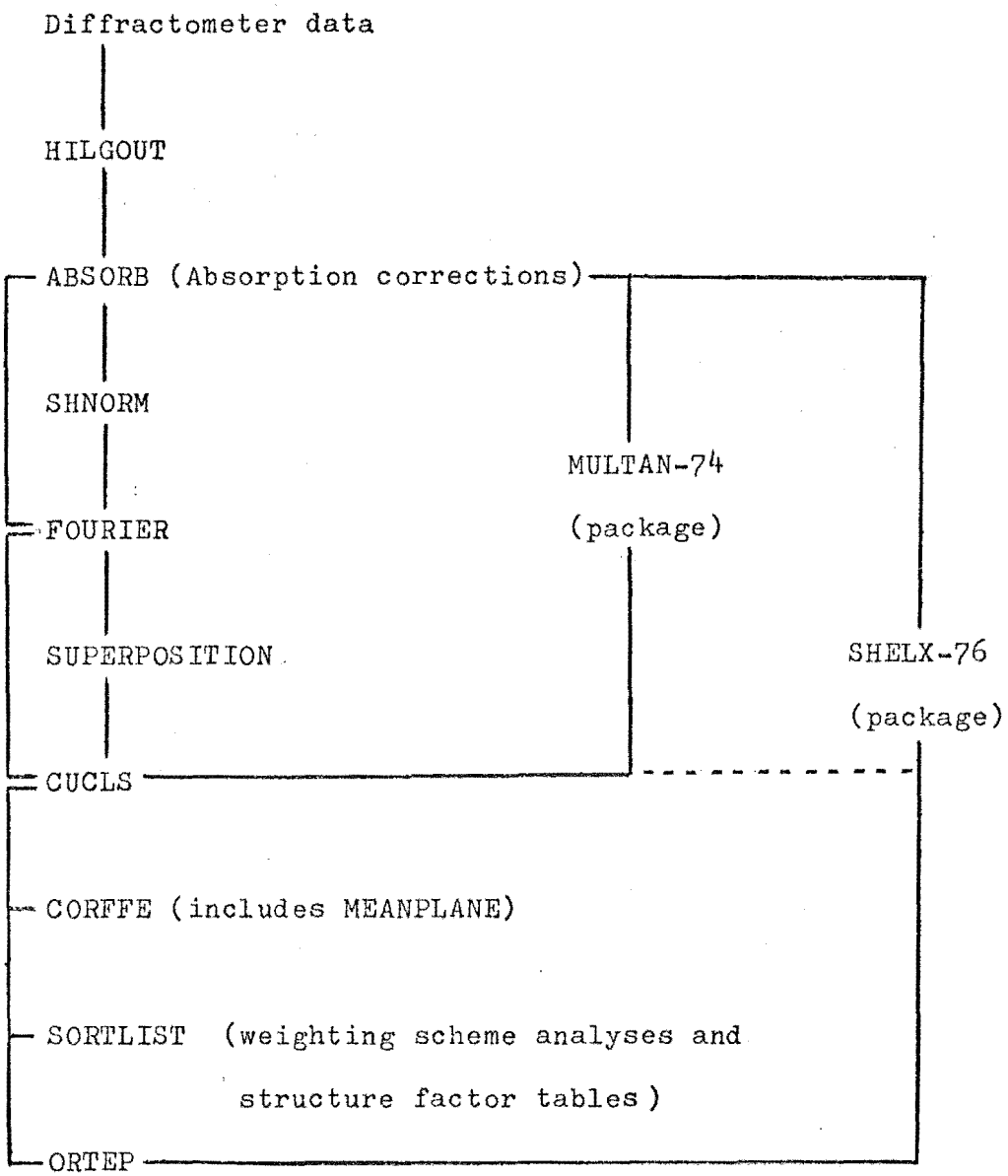


Table 8.2

Crystallographic Computing System (1977)



8.3.1 Conversion of Programs to the B6718 Computer

The approach which has been adopted in the implementation of programs is to concentrate initially on getting them just to execute, then to make them easy to use by simplifying the input and output, and finally, where the typical processing times warrant it, to minimise their execution costs by improving efficiency. The first stage is not always achieved as readily as is expected. There are several reasons for this. Firstly, few programs written for other machines are truely 'portable'. A notable exception is SHELX-76 (Sheldrick, 1975) which required only one trivial alteration before it would execute. The problem is compounded by the fact that Burroughs' Fortran is almost, but not completely, a super-set of the ASA standard (Heising, 1964). A second problem is the unusual (48 bit) word length of the B6718. (Integer variables are stored in sign-magnitude representation and require only 40 bits of each word.) This high precision means it is sometimes not possible to duplicate program executions from other machines where the input is identical. This can upset attempts to test and debug programs. The word length also causes problems in programs where run-time format editing is used and, occasionally, with data storage. Partial words for storing integer and logical variables are not supported on the B6700's. This can cause communication problems between the sub-programs in a program where COMMON blocks are specified differently and variables are declared as partial words. Errors introduced in this way when implementing IBM 360 or 370 programs can be particularly difficult to

locate. Such problems were particularly exasperating in the implementation of program SAP.

Character handling is often a problem when attempts are made to implement a Fortran program on a machine other than that for which it was originally written. This is not surprising since the language was designed with numeric computing only in mind. A small but frequently occurring problem peculiar to Burroughs Fortran is illustrated below:

```
      BLANK=' '
      IF (BLANK.EQ.'-')WRITE(6,10)
10    FORMAT ('EQUALITY IS SATISFIED')
```

This code, compiled and executed, has the unfortunate result of printing the message about equality. The .EQ. operator does not result in a full word comparison. Use of the .IS. operator, rather than the .EQ. operator, gives the desired result.

It was necessary for the author, a relatively inexperienced programmer when the project was initiated, to become quite familiar with the IBM 360/44 Fortran implementation in order to solve problems encountered with the conversion of the programs to the B6718. In the early days these problems were compounded by the inexperience of users, including the computer centre staff, with this machine. Also, the frequency and the nature of the changes made in each new release of the operating system. Furthermore, attempts to compile program CUCLS exposed several errors in the B6700 Fortran compiler of early system software releases.

Apart from getting the programs of Table 8.1 operational on the B6718, it was a major exercise to integrate them into a system usable by the entire research group. The approach adopted was to maintain a single copy of the codefiles of the most frequently used programs as permanent disk files. The other programs, and back-ups, were kept on magnetic tapes. Individuals use this common program library but store data files on their own tapes.

Program SUPERPOSITION illustrates how programs have been modified to make them more user oriented. This program is basically an aggregation of Hubbard and Jacobsen's (1969) programs GEN and ALS with a greatly simplified input. The programs formerly required the user specification of some parameters which are now obtained programmatically by reading a Fourier synthesis output file. A further unfortunate aspect of the original programs is the use of direct-access files which require specification of file attributes usually unfamiliar to inexperienced computer users. Burroughs Fortran allows dynamic allocation of file parameters which eliminated this problem. Unfortunately the author, herself, was not successful in her attempts to solve the structures of $C_6H_2(CCl_2)Ph_2$ and $C_{35}H_{42}O_6S_4$ using program SUPERPOSITION but her version has been successfully used, in this laboratory, by C.T. Page.

'It is widely conceded that B6700 programs written in Fortran do not as a rule execute as fast as comparable Fortran programs execute on less structured computer systems'... 'of comparable arithmetic and memory speeds' (Organick, 1973). This can be very true of X-ray crystallographic

programs. Optimising these programs with respect to turn-around time and cost usually means reducing processor time and, if possible, memory usage. The costs of input and output are usually small in comparison, as file-handling is invariably a simple sequential process.

The virtual memory management of the B6718 operating system can result in unfortunate segmentation of data structures (arrays and COMMON blocks) if they are larger than 1023 words. It is possible to specify their storage as a contiguous, unsegmented block of memory (LONG arrays) if they are of a total size of less than approximately 18,000 words*. A reduction of 50% in the execution time for program DABS was obtained by removing segmentation of a common block. System degradation can result when LONG arrays are used indiscriminately. This practice is discouraged by charging for actual memory used and refusing to run jobs of this nature except during certain periods of the day. As a consequence of this policy, found necessary to cope with the total demands on the system, large jobs are always run in low priority queues.

The implementation of the local crystallographic programs as described above, was a co-operative project directed from here but also involving crystallographers from the University of Auckland and the Chemistry Division of the D.S.I.R. The programs are currently being run on all five B6718 computers in the New Zealand Universities. The person responsible for any program additions or changes is expected to provide up-to-date user documentation. From time to time

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* The maximum depends on the particular installation.

new program versions are 'exported' from this laboratory. It is hard to separate the author's contributions in these areas from those made by others. She has worked on almost all the programs in Tables 8.1 and 8.2. Some of her major efforts are detailed in the rest of this chapter.

8.3.1a Implementation of the MULTAN74 Package

As an illustration of the problems typically encountered, the implementation of this package will be described in detail. No real attempts have been made to optimise the programs for this computer.

MULTAN74 (Main et al., 1974) is a suite of programs which may be used to develop preliminary structural models by direct methods from intensity data. Five programs from this package* have been implemented here:- NORMAL, MULTAN, FFT, SEARCH, and MFRP. With suitable alterations to appropriately specify files all but NORMAL and FFT could be compiled from the supplied source programs. To obtain successful executions, however, the following changes were made.

(i) NORMAL (The program which produces normalised structure factors.) Alterations to accommodate the local intensity data file format, a change of a function name, and replacement of the .EQ. operator by the .IS. operator in the free-format input routine were needed.

---

* DANFIG, developed locally as a non-plotting version of DANTEP, is part of the package but in this laboratory the file written by SEARCH is input to a version of ORTEP to produce the line-printer plots.

(ii) MULTAN (The direct methods program, updated from the 1971 version.) A few trivial alterations similar to those required for NORMAL.

(iii) FFT (The fast Fourier transform program.) This program would not compile because one subroutine referenced a data structure as a COMPLEX ARRAY whereas all the others accessed it as a REAL ARRAY. This problem was overcome by an EQUIVALENCE statement and the program compiled. Initial problems with executions were found to result from local variables in a subroutine assumed, incorrectly for this machine, to be of type OWN. (i.e. to remain unchanged from one subroutine call to the next.)

(iv) SEARCH (The program to perform a peak search on an E-Map.) Problems relating to word-size with the run-time formats had to be removed and some minor alterations made to output file so that it was compatible with program ORTEP.

(v) MFRP (A molecular fragment recognition program.) The only real problem was one of array bounds. The B6700 checks indices against the array bounds before referencing an array element.

8.3.2. Computer Programming for the PDP8/f Computer

In 1974 this laboratory obtained a PDP8/f computer with 8K ($K=1000_8$) words of core storage. This computer replaced the PDP8/I computer with 4K words of storage originally supplied with the Hilger and Watts diffractometer. Several years earlier a TENNECOMP cartridge unit had been acquired. The software supplied with the diffractometer, written in PAL/8 assembly language, had been considerably modified by

Dr. R.J. Dellaca especially to facilitate program storage and retrieval from this device.

An investigation, by the author, showed that optimum use of the additional 4K of memory of the new computer would require considerable re-structuring and re-programming of the diffractometer software. In particular, the section of code which handles interrupts in the four basic programs could not be readily modified to process interrupts generated during execution of code stored in the upper memory field. Re-writing of this module would have required extensive alterations to the programs. As the original software had been supplied only in the form of listings and binary (i.e. assembled) code, such alterations were not practicable.

The extra memory did enable important constants (orientation matrix, diffractomer reference points and cell parameters) to be retained between program loadings. This small feature helped to simplify setting-up procedures for automatic data collection.

The TENNECOMP device was replaced, in 1975, by a DEC magnetic-tape cassette reader with operating system CAPS/8. The Hilger and Watts software was modified to operate using cassettes for program storage. Because its software proved very inflexible the cassette system was replaced, late in 1975, by a twin-drive floppy-disk unit. The supplied operating system was OS/8.

The author directed the conversion of the software from storage on paper-tape to diskettes. Although the diffractometer programs execute in the lower 4K field, the upper field is essential for intermediate program and data

storage and retrieval. The original software was not designed to be run in conjunction with an operating system and it uses sections of memory normally not available to user programs.

In time it is hoped to convert some of the general calculations in X-ray structure analyses to the small computer for which there are suitable Fortran and PAL/8 programs available. Unfortunately the diskette drives have been out of action for considerable periods because of initial hardware problems. This has considerably limited further developments. Ultimately the normal transfer medium of intensity and other data, between the PDP/8 computer and the Burroughs B6718 may become the diskette rather than paper tape.

8.3.3 Initial Developments of a System for Interactive Terminals

Although terminals have been available at the University of Canterbury for some time, they have not been used routinely in structural analyses. There is currently a major problem of access. Because the present memory capacity of the B6718 is inadequate to support interactive terminal operation in addition to normal batch and remote batch entry activities, service to them has been restricted to two hours daily. While it is possible to edit files and to execute interactive programs which do not have large memory requirements, larger calculations must all be entered into the normal queues. This problem has considerably limited the nature of the developments undertaken, as well as

the enthusiasm for this type of computing. An additional memory module, to be installed in 1978, is expected to change this situation.

The software system for the interactive terminals is CANDE (Comment AND Edit language). It is still being developed by the Burroughs Corporation which means the available documentation is invariably out of date. In addition to possessing quite good string handling features, CANDE now enables most tasks which can be entered in batch mode to be initiated from an interactive terminal. The files used by CANDE are restricted to card-image type with EBCDIC coding.

It was decided to concentrate attention initially on the main-line activities of model refinement, extension and display, i.e. the programs FOURIER, CUCLS and ORTEP. Major modifications to program ORTEP so that it can be used to develop molecular displays on the DEC GT44 interactive graphics system, were part of a separate project undertaken by R.G. Holloway. The author's project was concerned specifically with programs FOURIER and CUCLS.

It was soon realised that it was not possible to execute these programs in an interactive mode because of their processing requirements, but with major modifications to the structure of their input and output files it would be possible to set up jobs for submissions into the normal queues from the terminals. The input files for these programs were of two types; binary files and 'card' (EBCDIC) files. The main binary files contained intensity data but atomic parameters could also be stored in this form. Because binary

files cannot be listed at a terminal they were no longer suitable for atomic parameters.

An analysis of the normal card input for these programs showed that much of this data was unchanged from run to run (eg. cell constants, and scattering factor tables). The variable input data included program control integers and, often, atomic parameters. It was decided to remove the constant data from these input files, thus reducing their size. This data is now stored at the beginning of the reflection data files. It is in character form so that it can be listed and modified directly from a terminal. The reflection data section on these files remains in binary form to avoid the unnecessary processing costs in interpreting formats every time it is read or rewritten. A small program has been written to set up this file and can be executed in either batch or interactive modes. A sample of an interactive execution dialogue is given in Figure 8.2. This style, with alternative batch and terminal inputs, is likely to be adopted in future local developments particularly for this type of program where execution involves minimal processing.

Once the constant data had been removed from the card (or pseudo-card) input to programs FOURIER and CUCLS the next step was to simplify the remaining input. It was decided that free-format input was very desirable and this has been based on a keyword structure. Free-format is advantageous provided it is accompanied by careful screening for invalid data and by the generation of explicit error messages. Care has been taken over these features. Both

```
R $CRYSTL/RETRIEVER;FILE FILE2=TJM/BRILS
#RUNNING 6166
GOOD AFTERNOON I HOPE YOU HAVE A GOOD SESSION
REMEMBER TO TERMINATE ALL FREE-FORMAT INPUT WITH THE LF KEY


PLEASE ENTER TITLE OF UP TO 60 CHARACTERS
#?
THYRSIFERYL ACETATE    C32 H55 O8 BR
IS THE SPACE-GROUP CENTRO SYMMETRIC? [ENTER YES OR NO]
NO
ENTER THE LATTICE TYPE [P,A,B,C,F OR I]
P
ENTER THE TOTAL NO. OF SYMMETRY CARDS[INCLUDE ONLY THOSE NOT
RELATED BY A CENTRE]
2
ENTER SYMMETRY CARDS ONE PER LINE IN INT. TABLES FORMAT
[   E.G.     X,1/2-Y,1/2+Z]
X,Y,Z
MISSING COMMA[S] IN SYMMETRYCARD
ENTER SYMMETRY CARDS ONE PER LINE IN INT. TABLES FORMAT
[   E.G.     X,1/2-Y,1/2+Z]
X,Y,Z
-X,1/2+Y,-Z
ENTER 6 CELL CONSTANTS
12.348 12.055 12.166 90 107.314 90
DO YOU REQUIRE ANOMALOUS SCATTERING FACTORS FOR ANY ATOMS ?
    [ENTER YES OR NO]
YES
DO YOU WANT COPPER[CU] OR MOLYBDENUM[MO] RADIATION ?
CU
ENTER THE CORRECT SYMBOLS FOR THE ANOMALOUS SCATTERS
    [E.G. CL,S,FE,ETC.]
BR
DATA FOR    BR     WRITTEN ON FILE  WITH CU     ANOM. DISP.
ENTER THE CORRECT SYMBOLS FOR ALL NON-ANOMALOUS SCATTERERS
    [ EG. H,CL,F,F-,MG2+ ETC.
C H O
DATA FOR    C      WRITTEN ON FILE
DATA FOR    H      WRITTEN ON FILE
DATA FOR    O      WRITTEN ON FILE


#ET=3:01.7 PT=2.3 IO=3.5
```

Figure 8.2

A sample execution, in the interactive mode,

of the program which sets up the file

of constant data

programs can be executed from a single file which is convenient for terminal operations. These developments have mainly been programmed in Burroughs Extended Algol. Apart from the greatly increased facility in handling character data, there are useful file and task handling features in this language which are not available in Fortran. Code files for procedures compiled in Algol can be linked into code compiled from a Fortran source.

An illustration of the changed input form for these programs is given below:-

FMAP 1

LIMITS 0 .5 0 .5 0 .5 .3 .3 .3 X

(Characters underlined are those in the keyword which must be given.)

These two cards could be used to initiate a difference Fourier calculation in, for example, space group $P2_12_12_1$ to produce interpolated co-ordinates for 50 (a default) peaks. The original form of input required 10 strictly formatted cards to accomplish the same task. The similarity of the input data cards to those of SHELX-76 was quite intentional.

The key feature which has simplified the input for programs CUCLS, apart from the removal of the constant data and the use of free-format, is the elimination of the parameter selection cards. Previously each parameter had to be specified as to whether or not it was invariant. This was a source of many errors in setting up input decks for program CUCLS. In the new version the program assigns the most likely control codes for each parameter unless

these are specifically designated by the user (eg. for atoms on special positions).

Thus it may be seen that a start has been made in setting up a system of programs to be run from interactive terminals. Ultimately almost all the programs in the library may be adapted, similarly, so that their execution may be initiated from such terminals. Before such developments are likely, however, a considerable improvement will be required in the service provided to interactive terminals. Regardless of whether this happens, the new and simplified form of input for programs FOURIER and CUCLS should benefit users in normal batch mode operations.

CHAPTER 9

CONCLUDING COMMENTS

In common with most research projects this one has had its successful and unsuccessful aspects. It was disappointing not to solve all the structures attempted. The precision of the results of the successful analyses was also disappointing although, in some cases, not unexpected. However, the eventual determination of the structure of 1,1-dichloro-2,5-diphenylcyclopropabenzene was particularly pleasing and most informative. It is interesting to note that subsequently other workers in this laboratory have had difficulties solving structures of similarly sized organic molecules using chlorine as a 'heavy atom'. The correct structure has often been revealed, in these cases, by the first 'black-box' application of a direct methods program such as MULTAN. Although, in this particular analysis, the solution was not obtained quite so easily from direct methods it would seem that these can provide a better first approach in such circumstances.

The other analyses, where the space group was non-centrosymmetric, were also challenging, although one was solved using vector methods. It is apparent that in some cases high quality data is as essential for the structure solution itself by direct methods, as it is to low errors in refined (and derived) parameters in the solved structure. In this respect the unsolved structure of the compound of probable empirical formula $C_{15}H_{12}N_4$, is vexing. The

author feels that, with the fairly good intensity data collected and given sufficient time and money, its structure would be solved. Further, a good set of intensity data for the dinitro,methyl imidazole compound should readily yield a structure solution.

Chemical crystallography is now considered to be divided into two categories: 'analytical crystallography' and 'structural crystallography'. These classes have been defined as follows:-* 'analytical crystallography is primarily a tool for determining rapidly and conclusively, the gross structure of a molecule and particularly its atom connectivity; structural crystallography is concerned with the details of molecular geometry and relating them to theories of chemical bonding and electron distribution'. Only one of the six analyses undertaken, that of 1,1-dichloro-2,5-diphenylcyclopropabenzene, comes into the latter category. Viewed in this light, the limited precision of the other three analyses is of secondary importance to the unequivocal determination of the atom connectivity in these molecules; the initial reason for undertaking the analyses.

The high R-factors obtained were to be expected in two of these analyses because of the poor quality of the crystals used. Further contributory factors were the

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*'Status and Future Potential of Crystallography', the report of a conference sponsored by the U.S.A. National Committee for Crystallography of the Assembly of Mathematical and Physical Science of the National Research Council, 1976,p.13.

limitations imposed on the structural models. Financially it is no longer possible, in this laboratory, to develop all structural models fully and then to refine the resulting parameter set to convergence. This is particularly the case where the model requires many parameters and converges only slowly as is commonly found where the space group is non-centrosymmetric. To help reduce computing costs it has become a standard laboratory practice to use only those data for which $F_o^2 \geq 3\sigma(F_o^2)$ in refinements unless there are very strong reasons for doing otherwise.

In some ways the programming part of this project was the most significant aspect. While no new large programs were contributed to the overall computing system for either the Burroughs B6718 or the PDP8/f computers, the contributions made in this area are having significant effects on crystal structure analyses particularly in most other New Zealand universities. It is essential for programs of this type to be as free from error and as well documented as is practicable. This was especially important with the Hilger and Watts' software changes; firstly because they are written in less readily decipherable assembly language and secondly because they were required to make the Hilger software compatible with the operating system now used.

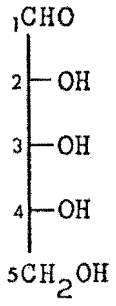
At the beginning of this project the author's knowledge of computer science was as shallow as it was of crystallography. It was confined to simple scientific Fortran programming. In the course of the project it has gradually been extended to an understanding of more general high and low level programming techniques, operating

systems and some data-base management concepts. This is a key reason why the developments have proceeded so slowly.

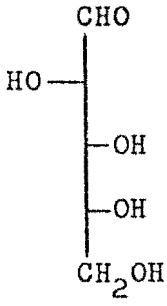
It seems likely that much more use will be made in this laboratory in the future of X-ray structure analysis packages such as SHELX-76. This package does not have all the flexibility of the extensive suite of programs developed here over the years, and it has not been optimised for the B6718 computer. Consequently, at some stage in the majority of structure analyses, the local programs will be used. In particular optimised versions of the fast program, CUCLS, will be used in final refinements where its new style of input should be very beneficial.

Appendix 1

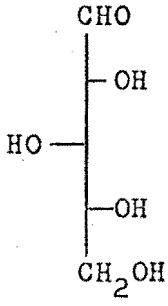
Acyclic Forms of the D-series of Aldoses



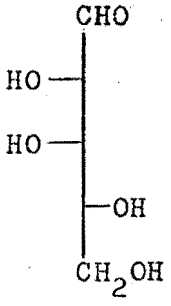
ribose*



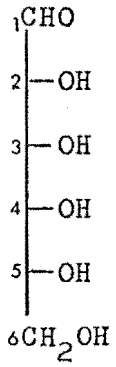
arabinose



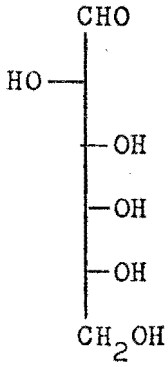
xylose



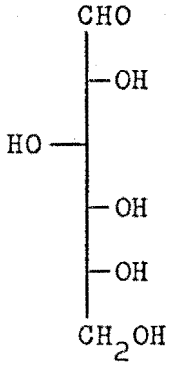
lyxose



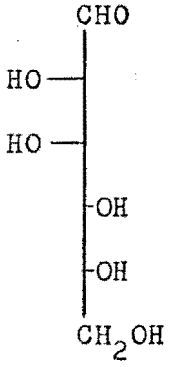
allose*



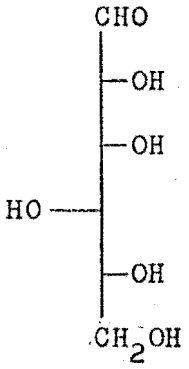
altrose



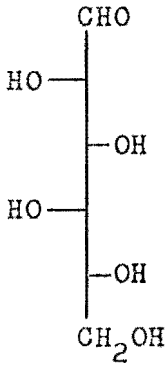
glucose



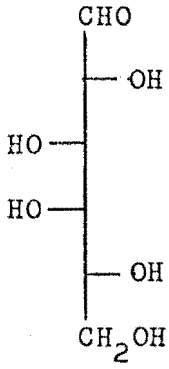
mannose



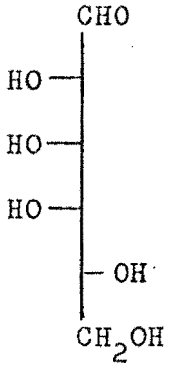
gulose



iodose



galactose



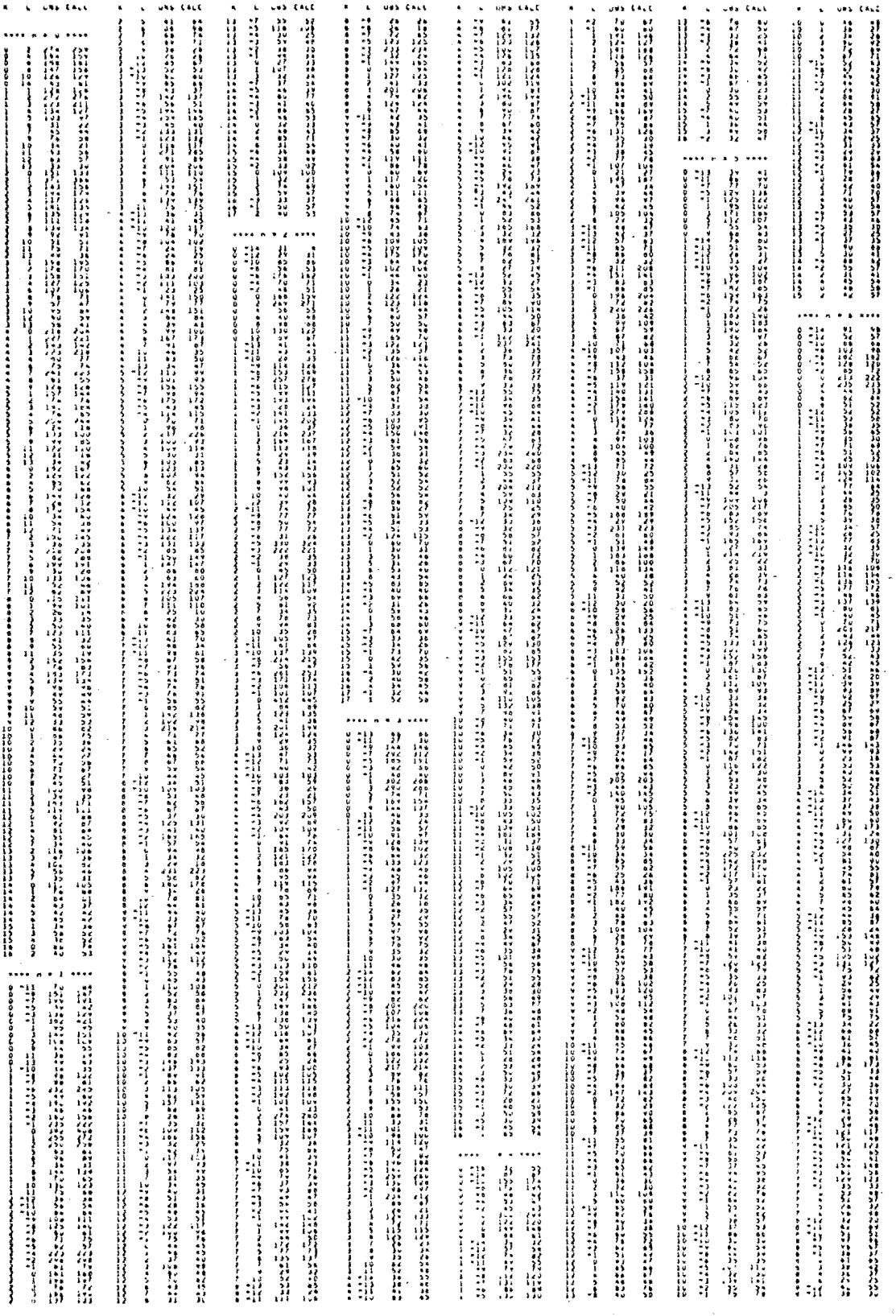
talose

* Usual numbering of the carbon chain is indicated.

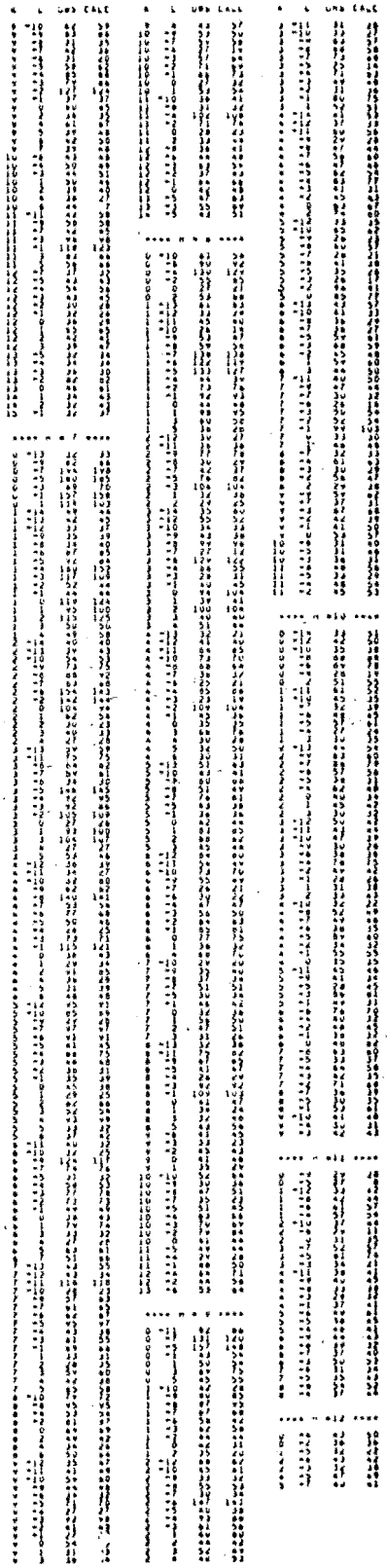
Appendix 2

Observed and Calculated Structure Amplitudes

for $(AsPh_3)_2\overline{PtCF_2CFCFCF_2}$



Appendix 2 contd.



Appendix 3

Observed and Calculated Structure Amplitudes for $C_6H_2(CCl_2)Ph_2$

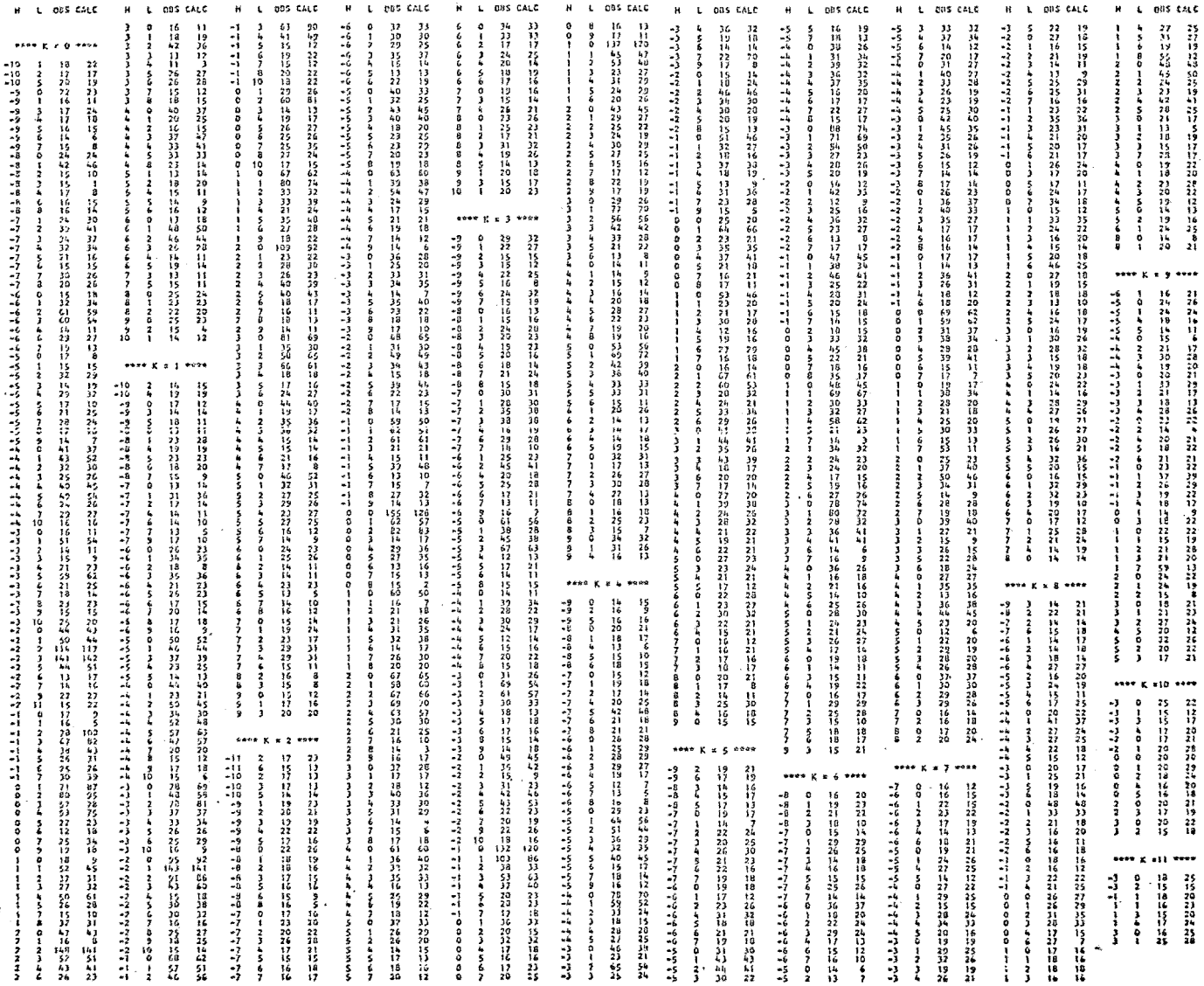
Appendix 4

Observed and Calculated Structure Amplitudes for $C_{35}H_{42}O_6S_4$

Appendix 4 contd.

Appendix 5

Observed and Calculated Structure Amplitudes for $C_{32}H_{55}O_8Br$



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